



## 저작자표시-동일조건변경허락 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.
- 이차적 저작물을 작성할 수 있습니다.
- 이 저작물을 영리 목적으로 이용할 수 있습니다.

다음과 같은 조건을 따라야 합니다:



저작자표시. 귀하는 원저작자를 표시하여야 합니다.



동일조건변경허락. 귀하가 이 저작물을 개작, 변형 또는 가공했을 경우에는, 이 저작물과 동일한 이용허락조건하에서만 배포할 수 있습니다.

- 귀하는, 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리는 위의 내용에 의하여 영향을 받지 않습니다.

이것은 [이용허락규약\(Legal Code\)](#)을 이해하기 쉽게 요약한 것입니다.

[Disclaimer](#)

도시계획학 석사학위논문

Comparison of polybrominated diphenyl  
ethers concentration in indoor air of  
office, laboratory, and internet café.

- Based on the prediction using modified Integrated Indoor Air  
Quality Model -

Dec. 2012

Environmental Planning  
Graduate School of Environmental Studies  
Seoul National University  
Wu Chao

# Comparison of polybrominated diphenyl ethers concentration in indoor air of office, laboratory, and internet café.

- Based on the prediction using modified Integrated Indoor Air  
Quality Model -

지도교수 이동수

이 논문을 도시계획학 석사학위 논문으로 제출함

2012년12월

서울대학교 환경대학원

환경계획학과

오 초

오초 도시계획학 석사 학위논문을 인준함

2012년12월

위 원 장 \_\_\_\_\_(인)

부위원장 \_\_\_\_\_(인)

위 원 \_\_\_\_\_(인)

## ABSTRACT

The harmfulness of PBDEs are widely understood and the indoor air is the one of main exposure path of PBDEs to human. In spite of this, there is few monitoring data of PBDE concentration level in indoor environment in South Korea. Thus, in this research, it is expected to compare the air quality in home, research office and internet cafe, and find out how the main factors affect the concentration level of PBDE via model simulation.

In order to predict the concentration level of PBDEs, Integrated Indoor Air Quality (IIAQ) model, which is developed for prediction of Semi-volatile organic compounds(SVOCs), is used. The model is modified for this research. The main revised contents are: emission rate are modified as the function of temperature; The ventilation period is modified to be selectable. The modified IIAQ model is evaluated by comparing the predicted value and measured data. BDE 47, BDE 99, BDE100 are selected as the research targets. In the model, the simulation condition are set as that home volume is  $5*3*3\text{ m}^3$  with one emission source (computer), laboratory volume is  $9*5*3\text{ m}^3$  with 10 emission source and internet cafe volume is  $15*10*3\text{ m}^3$  with 55 emission source.

Comparing the predicted value and measured value of BDE 47, BDE 99, BDE 100 by modified IIAQ model, The uncertainty is in the range of  $\pm 100\%$ . With the environment condition above, Average BDE 47 concentration in steady status are  $22\text{pg}/\text{m}^3$ ,  $110\text{pg}/\text{m}^3$ ,  $938\text{pg}/\text{m}^3$  in home, research office and internet cafe respectively. For BDE 99, the average concentration are  $17.1\text{pg}/\text{m}^3$ ,  $33\text{pg}/\text{m}^3$ ,  $132\text{pg}/\text{m}^3$  and for BDE 100, the average concentration are  $5.6\text{pg}/\text{m}^3$ ,  $29.3\text{pg}/\text{m}^3$ ,  $283\text{pg}/\text{m}^3$  in each indoor environment via prediction. According to the results, the average concentration of Penta-BDEs in internet cafe is about 50 times higher than which in home. Assumed that exposure time is constant, internet cafe is the location with the highest risk of human exposure to Penta-BDEs. As the one of important factor which affect the PBDEs concentration in indoor environment, constantly use of computer leads to 9~13 times higher Penta-BDEs concentration level than which computers are constantly not in use for the reason that higher internal temperature of emission source leads to higher volatilization rate of PBDEs. The effect of ventilation process on reduction of PBDEs is depends on the differences with indoor and ambient PBDEs concentration. Thus, due to the low level of Penta-BDEs concentration at home, the effect of ventilation is not obvious; In contrast, the air exchange effect on reduction of Penta-BDEs in laboratory and internet cafe is considerable, which are predicted as 11.3% and 45% reduction effect separately with the air exchange rate of 0.5/day, due to huge differences of Penta-BDEs concentration level

in indoor and ambient. In addition, 100 times higher Penta-BDEs concentration in ambient than which the value from literature leads to obviously increase of Penta-BDEs concentration level in indoor environment. In comprehensive, the reason that the high exposure risk in internet cafe is because of the big number of computer and constantly use of computer. Even that ventilation process would reduce considerable PentaBDEs concentration in internet cafe, the concentration level of Penta-BDEs may still high.

Since that computer is assumed as the only emission source of Penta-BDEs in indoor environment, thus the density of computer, and use of computer comes as the main factors affect the indoor air quality. Use of computer leads to about 10times increase of Penta-BDEs concentration level, Thus, computer is better to be shut down when it is not necessary to be used not only for the view of energy saving, but also for reducing the risk of human exposure to Penta-BDEs. If constantly use of computer is necessary, frequently exchange of air would be help to reduce the risk of human exposure to Penta-BDEs.

Key words: PBDEs, Penta-BDEs, Polybrominated dipenyl ethers, indoor, concentration, indoor model

Student number: 2010-24185

## <Contents>

<b>1. Introduction</b>	<b>1</b>
1. Research objective and background	1
2. Research scope	3
3. Research method	4
4. Scheme of this study	5
<b>2. Literature review</b>	<b>6</b>
1. Polybrominated diphenyl ethers	6
1) Physical properties	6
2) Source and distribution	7
3) PBDEs in indoor environment	8
2. Integrated indoor air quality model	9
<b>3. Materials and method</b>	<b>13</b>
1. Chemical properties	13
1) Material-air partitioning coefficient	13
2) Particle-air partitioning coefficient	14
3) Henry's Law constant	15
4) Vapor pressure	16
2. PBDE concentration	18
1) PBDEs concentration in atmosphere	18
2) PBDEs concentration in indoor space(air)	19
3. Indoor space	21
1) Space information	21
2) Furniture information	22
<b>4. Modification of Integrated Indoor Air Quality model</b>	<b>25</b>
1. Emission rate	25
2. Vapor-particle coefficient	29
2. Wall compartment	30
3. PBDEs concentration in ambient	30

4. Air exchange .....	30
<b>5. Model evaluation .....</b>	<b>32</b>
Estimation .....	32
<b>6. Results and discussion .....</b>	<b>36</b>
1. Particle size distribution .....	37
2. Flux analysis .....	38
1) concentration pattern .....	38
2) Emission .....	40
3) Wall compartment .....	42
4) Natural ventilation and air exchange .....	44
5) Deposition .....	46
3. Ventilation effect .....	48
4. Effect of Computer operation .....	50
5. Temperature in indoor environment .....	51
6. Outdoor concentration .....	52
7. PentaBDE concentration in indoor space .....	54
1) BDE47 .....	54
2) BDE99 .....	60
3) BDE100 .....	62
<b>7. Conclusion .....</b>	<b>64</b>
■ Reference .....	66

## <Table Contents>

<Table 1-1> Estimated world market demand for PBDEs, TBBPA and HBCD in 1999 · 2	
<Table 3-1> Octanol-air coefficient for BDE congeners ······ 13	13
<Table 3-2> Material-air coefficient for BDE congeners ······ 14	14
<Table 3-3> Vapor-Particle partitioning of PBDEs from reference ······ 15	15
<Table 3-4> Henry's Law constant of PBDEs from reference ······ 16	16
<Table 3-5> Vapor pressure of target BDE congeners from reference ······ 17	17
<Table 3-6> Basic information of 3 different indoor environment ······ 21	21
<Table 3-7> Surface area of furniture,(internet information) ······ 23	23
<Table 3-8> Result of survey from the students of seoul national university, 2012. 5 · 24	24
<Table 5-1> Measured value from reference ······ 35	35
<Table 7-1> Simulation condition for South Korea ······ 53	53



<Figure contents>

<Figure 1-1> Scheme of this study .....	5
<Figure 2-1> Chemical structure of PBDEs .....	7
<Figure 2-2> Air flow of previous Integrated Indoor air quality model .....	10
<Figure 3-1> PBDE outdoor concentration in south Korea by congeners .....	18
<Figure 3-2> Comparision of PBDEs concentration in vapor phase(Vorkmap 2010, Toms et al,2009,Thuresson et al. 2011, Wijesekera 2004) .....	19
<Figure 4-1> Conception of modified Integrated Indoor air quality model .....	26
<Figure 4-2> logKoa calculation by temperature. ....	32
<Figure 5-1> Compare of Predicted value and reference value of BDE 47 .....	33
<Figure 5-2> Compare of Predicted value and reference value of BDE 99 .....	34
<Figure 5-3> Compare of Predicted value and reference value of BDE 100 .....	37
<Figure 6-1>modeled indoor chemical mass distribution from home .....	39
<Figure 6-3> (a) Particle phase BDE 47 concentration variation within 3days .....	41
(b) Vapor phase BDE 47 concentration variation within 3days	
<Figure 6-4> (a) volatilization flux from computer slab .....	43
(b) Absorption flux to computer slab	
<Figure 6-5> (a) BDE 47 flux from wall .....	45
(b) BDE 47 flux to wall	
<Figure 6-6> (a) Natural ventilation flux of BDE 47 .....	47
(b) Air exchange flux of BDE 47	
<Figure 6-7> Deposition flux of BDE 47 .....	49
<Figure 6-8> (a) BDE 47 concentration with computer off and ventilation .....	52
(b) BDe 47 concentration with computer operation and ventilation	
<Figure 6-9> BDE 47concentration with computer operating and off .....	50
<Figure 6-10> Indoor temperature effect on BDE 47 concentration .....	51
<Figure 6-11> Outdoor BDE 47 concentration affect the indoor BDE 47 concentration	52
<Figure 6-12> Emission rate of BDE 47 at home, office and internet cafe .....	55
<Figure 6-13> Concentration of BDE 47 at home, office and internet cafe .....	57
<Figure 6-14> Concentration of BDE 99 at home, office and internet cafe .....	60
<Figure 6-15> Concentration of BDE 100 at home, office and internet cafe .....	62

# **I . Introduction**

## **1. Research objective and background**

Polybrominated diphenyl ethers (PBDEs) are a major class of additive brominated flame retardants that have been widely used in considerable product, for example, textiles, electronics and plastics. PBDEs are one group of Brominated flame retardants that additives mixed into polymers and are not chemically bound to the plastic or textiles and may separated or leach from the surface of their product into environment (de Wit, 2002). Because of extensive use in the past decades, PBDEs have increased exponentially in environmental matrixes (de Wit, 2002; Hites, 2004; Oros et al., 2005). Recent data calls to concerns on PBDE congeners for the reason that they are identified as endocrine-disrupting chemicals, which have potential to evidence indicates that PBDEs may possess liver toxicity, thyroid toxicity, and neurodevelopmental toxicity (EPA, 2006). Due to environmental safety and persistence of PBDEs, the studies of the processes that transport and transform these chemicals in the environment has been prompted (Chen et al., 2007). PBDEs are distributed to most areas among the world, these chemicals can be found in Atmosphere, water, sediment, biota, food and human being, There are several routes of human exposure, the main route is considered as through diet. The dust collected from inside television sets and parliamentary buildings, and an internet provider, in total eight countries (Leonards et al., 2001) contains high level of PBDEs. As PBDEs emits into the indoor air, it may adsorb to surfaces and particles (Waye, 2008) which leads to human exposure to PBDEs. According to the research, the highest

concentration is investigated in the workplace room equipped with number of computers, it is claimed indoor exposure responsible for about 27% human exposure to PBDEs.

According to (Kim, 2001), People in South Korea spend 95.4% time in indoor space, which lead to extremely high possibility that human exposure to harmful chemical compounds that ubiquitous in indoor environment. Even that, currently, there is no regulations target to PBDEs in world scale. Europe parliament has already claimed that defer to use any kinds of product contains PBDEs from 2006 unless these chemical group to be proved harmless (EPA, 2002).

Currently, there are only a few of specific regulation concerns on PBDEs. On June 1, 2006, California state began prohibiting the manufacture, distribution and processing of flame-retardant products containing penta-BDE and octa-BDE. In June 2008, the U.S. EPA set a safe daily exposure level ranging from 0.1 to 7ug per kg body weight for 4 most common PBDEs ([www.epa.gov/iris](http://www.epa.gov/iris)). In April 2007, Washington state passed a bill that banning the use of PBDEs. In May 2007, the legislature of the state of Maine passed a bill phasing out of use of DecaBDE.

Table 1-1: Estimated world market demand for PBDEs, TBBPA and HBCD in 1999 given in metri tons([www.bsef.com](http://www.bsef.com))

	PeBDE	OcBDE	DeBDE	TBBPA	HBCD
Americas	8290	1375	24300	21600	3100
Europe	210	450	7500	13800	8900
Asia	0	2000	23000	85900	3900
Total	8500	3825	54800	121300	15900

The European Union determined to phase out the use of PBDEs in electric and electronic devices. This ban was formalised in the RoHS directive, and an upper limit of 1g/kg for the sum of PBDEs was set. In

February 2009, the institute for Reference Materials and Measurements (IRMM) released two certified reference materials (CRMs) to help analytical laboratories better detect this class of flame retardants. Some products that have a long consumer life are a continuing source for some of the lower congeners, and there is some concern that the deca-products may break down into lower, and more harmful, congeners (Stapleton and Doder, 2008).

However, In South Korea, Currently, no specific regulation targets to PBDEs control. After South Korea became a member of Stockholm agreement next year, it is possible that PBDEs become a prohibited class of POPs chemical compound in South Korea.

Purpose of this study is predicting concentration of PBDEs in different typical indoor environment in South Korea, understanding factors which affect concentration of PBDEs indoor environment and find out which is the high risk location for human exposure to Penta-BDEs

## **2. Research Scope**

Among 209 kind congeners of Polybrominated diphenyl ethers, BDE47, BDE99 and BDE100 are most frequently used and detected in different electrical and electronic products, and reported in the many papers and thesis, which are the target of this study.

This thesis mainly focus on PBDEs in indoor environment. Since PBDEs emitted mainly from Computer and TV set in indoor environment. Hence, it

is important to investigate the place that contains these two electronic equipment. According to (Wijesekera, 2002), the research target was grouped by workplace and house.

In this thesis, it is divided indoor environment into house, research office and internet cafe.

### **3. Research method**

Integrated indoor air quality (IIAQ) model is used for Predicting VOCs and Certain SVOCs (PAHs and PBCs). As one kind of SVOCs, it is possible to predict PBDEs concentration in indoor environment via IIAQ model. However, certain modification of IIAQ model is necessary for predication of PBDEs, since there are still many differences in chemical properties between PBDEs and other SVOCs in spite of they are considered to be similar.

Then modified IIAQ model should be estimated to prove its precision. The prediction results are compared with monitored value from published papers to check that the model is predicable or not. After estimation, modified IIAQ model can be applied to home, laboratory and internet cafe separately for understanding what are the factors affect Penta-BDEs' concentration and the concentration level of BDE 47, 99, 100 in these indoor environment.

#### 4.Scheme of this study

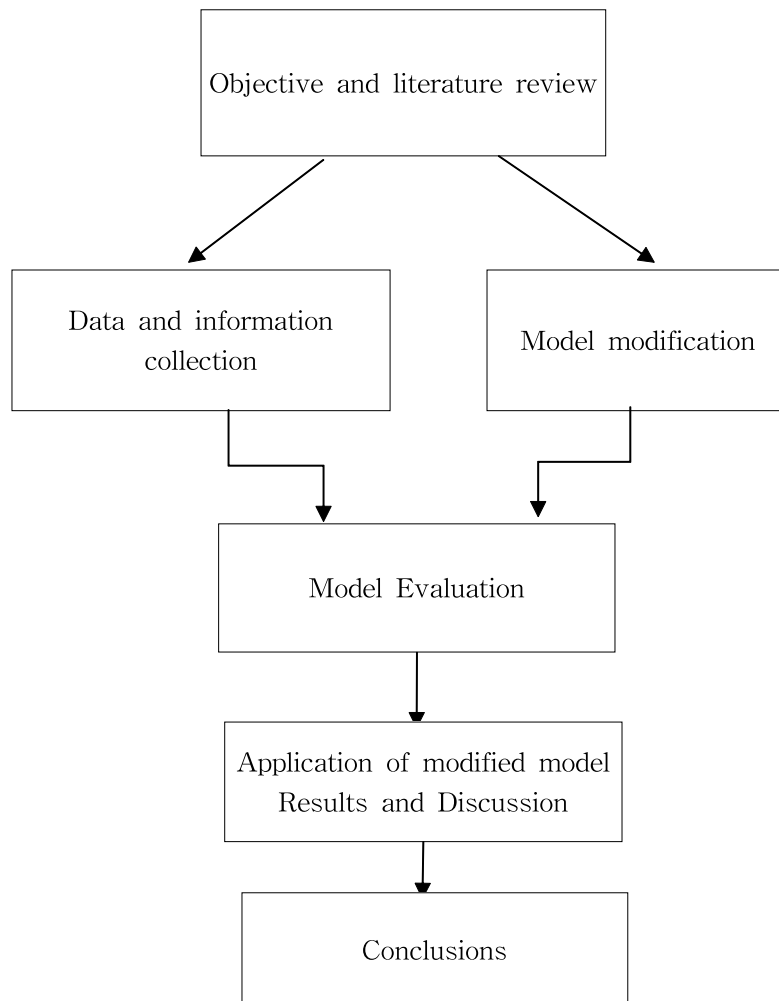


Figure 1-1. Scheme of this study

## II. Literature review

### 1. PBDEs

#### 1) Physical properties of PBDEs

PBDEs has 209 congeners, major Consumer products with PBDEs are usually contains pentaBDEs, octaBDEs and DecaBDEs. The Penta-products BDE47, BDE 99, BDE 153 and BDE 154 in a ration of 9:12:2:1 (Hale et al., 2001; Sjodin et al., 1998). The Octa-products contain Hexa-to Nona-brominated congeners, and the Deca-products are almost all decabromodiphenyl ether (BDE209). The commercial PBDEs products composition has been presented by WHO 1994. PBDEs are persistent, bioaccumulating environmental pollutants which are similar to polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polycyclic aromatic hydrocarbons (PAHs). (Cetin et al., 2005). The water solubilities and vapor pressures of PBDEs are relatively low and therefore, they are incline to adsorb onto solid particles(i.e., sediment, soil, atmospheric particles) when they are released into environment. Because of their high lipophilicity and resistance to degradative processes, PBDEs are expected to bioaccumulate easily (D'Silva, 2004). In addition, PBDEs have low vapor pressures, with logKowS (octanol-water partitioning coefficients)in the range 5.9-6.2 for TeBDEs, 6.5-7.0for Penta-BDEs, 8.4-8.9 for Octa-BDEs and 10 for Deca-BDE (Watanabe and Tatsukawa, 1990).

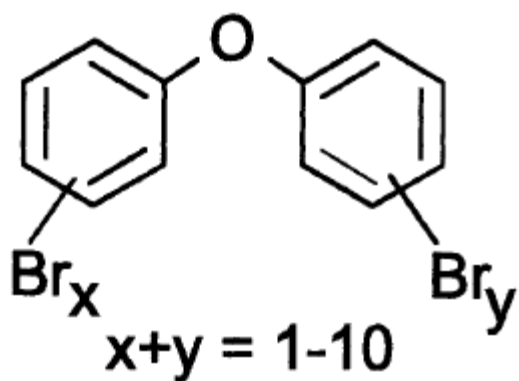


Figure 2-1: Chemical structure of PBDEs

## 2) Sources and distribution of PBDEs

Polybrominated diphenyl ethers (PBDEs) are flame retardants used in polymers, paints, textiles, and plastic housings of electronic products such as TV sets and computers, car parts, electric components and cables so as to improve the fire preventative abilities of products. (de Wit, 2002; Hyotylainen and Hartonen, 2002). Hence, they are widely used all over the world. Annual worldwide production of penta-, octa- and deca-BDEs technical products in 1990 was estimated to be 4000, 6000, and 30000 metric tons, respectively (Arias, 1992). Table 2-1 shows that world demands for brominated flame retardants. Besides of electrical product, electronic waste is the major source of PBDEs as well. Every year, 20-50 million tones of Electronic waste are generated world-wide (DEWA-GRID0 Europe, 2005). Most of these E-waste is being transported to Asia.

Refers to (KEI, 2001), the use of flame retardants has been steadily increasing,



by almost 10% per year during last decade in Korea. Brominated flame retardants (BFRs) is accounting for about 56% of total flame-retardant. The consumption of BFRs in Korea in 2002 was 49050 tons (KISTI, 2002). Deca-BDEs owes major proportion of total flame-retardant market, while Penta-BDEs and Octa-BDEs accounts for minor proportion of the total flame-retardant market (KISTI, 2002).

### **(3) PBDEs in indoor environment**

PBDEs are detected in indoor air according to many papers, especially sorbed to aeryly suspended dust inside homes and office buildings (EPA, 2010). Human live in indoor environment with polluted dust is the primary way in which human become exposed. Back casing of television sets ; the casings to personal computers (PC); facsimile machines, printers and so forth are contains PBDEs. PBDEs may volatilize from these products and pollute indoor air through using them. For instant, Volatilization of BDE 47, BDE 100, BDE99 and BDE 85 from a computer work station has been observed (Kemmlein et al., 2003); Another study conducted in office buildings determined a qualitative association between the presence of products contains PBDEs and subsequent levels of PBDEs in indoor air (Harrad et al., 2008).

PBDEs volatilized from products into surrounding air. A mount of PBDEs volatilized would be expected to partition between vapor and particle phases. Increased sorption to dust particles in air and increased degree of bromination of the molecule. Partitioning is enhanced by organic fraction of dust, and this creates a homogeneous distribution of PBDEs in indoor dust particles (Webster et al., 2009).

Indoor air levels of PBDE contaminated dust are considered to be highly variable from one indoor environment to another. Such variability is caused by

age and numbers of PBDE-treated materials within the indoor spaces and ventilation rate, the rate of fresh air exchange with in the indoor spaces, and the active use of PBDE treated products and materials (Hazrati and Harrad, 2006).

## 2. Integrated Indoor Air Quality model

Integrated indoor air quality (IIAQ) program is the microenvironment model that combines all elements in one space. Especially, this model divided one space into air compartment and material compartment, each compartment is applied by mass balance principle. And this model can consider both vapor phase and particle phase simultaneously of a certain chemicals, which is the reason why the model is considered adapted in this study.(Figure 2-2)

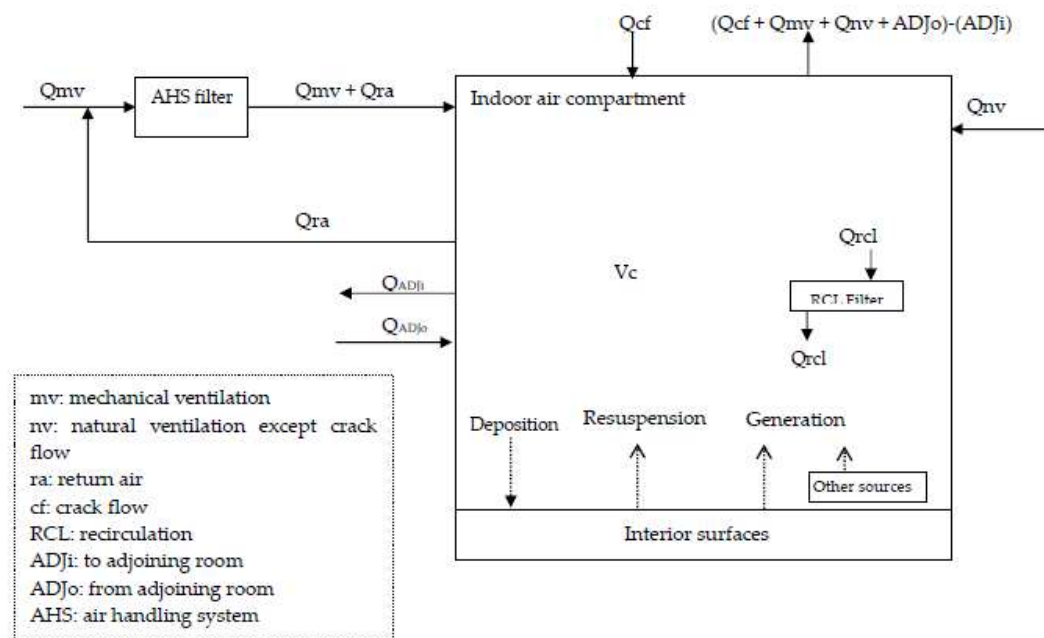


Figure 2-2. Air Flow of Previous IIAQ model

In this model, the input mass of particles through inflow, generation and resuspension is equal to the output mass of particles through outflow, deposition and filtration, and assume that there is no reaction between particles. The equation used in this model shows as following;

(1)particle side:

$$\begin{aligned}
V_c \cdot dM(d)/dt &= (all\ P\ inputs\ via\ air\ inflow) - (all\ P\ loss\ via\ air\ out\ flow) - (P\ indoor\ loss) \\
&+ (P\ indoor\ generation + P\ resuspension) \\
&= [Q_{mv} \cdot M_o(d) + Q_{ra} \cdot M(d)] \cdot (1 - fE(d) + Q_{cf} \cdot M_o(d) \cdot P(d) + Q_{nv} \cdot M_o(d) + Q_{ADJo} \cdot M_{adj}(d) \\
&\quad (all\ P\ inputs\ via\ air\ inflow) \\
&- [(Q_{mv} + Q_{ra} + Q_c + Q_{nv} + Q_{ADJo}) - (Q_{ra} + Q_{ADJi}) + Q_{ra} + Q_{ADJi}] \cdot M(d) (all\ P\ loss\ via\ air\ out\ flow) \\
&- [\sum_i A_i \cdot V_{d,i}(d) \cdot M(d) + Q_{rcl} \cdot (1 - fE_{rcl}) \cdot M(d)] \\
&\quad (P\ indoor\ loss (= deposition + recirculation\ filtration)) \\
&+ [S_g(d) + S_{res}(d)] (P\ generation\ and\ resuspension)
\end{aligned}$$

Vd: velocity of deposition

Eg(d): generation rate

Eres(d): resuspension rate

(2) Vapor side:

$$\begin{aligned}
Vdc/dt &= [(Q_{mv} + Q_{cf} + Q_{nv}) \cdot C_{vo} + Q_{ADJo} \cdot C_{vADJo} + Q_{ra} \cdot C_v] (inputs\ via\ air\ inflow) \\
&- [(Q_{mv} + Q_{ra} + Q_{cf} + Q_{nv} + Q_{ADJo}) - (Q_{ra} + Q_{ADJi}) + Q_{ra} + Q_{ADJi}] \cdot C_v (outputs\ via\ air\ inflow) \\
&- [(surface\ interaction\ rate) + V_c \cdot k_v \cdot C_v] (indoor\ loss (= surface\ interaction + reaction)) \\
&+ [E_{vg}] (indoor\ generation)
\end{aligned}$$

Vc: total volume of target space.

M(d), M<sub>o</sub>(d) and M<sub>adj</sub>(d): mass concentration of adjoint indoor and outdoor space

Q<sub>mv</sub>: air flux from outdoor

Q<sub>ra</sub>: return air flux

Qcf: air flux from crack flow  
Qnv air flux from natural ventilation except crack flow  
QADJi: air flux from adjoining room  
Qrcl: air flux from recirculation  
fE: efficiency of air handling system  
fErcl: efficiency of recirculation  
P(d): penetration factor  
Ai: size of inside skin

### 3. Materials and method

#### 1. Chemical property

##### 1). Material–Air partitioning coefficient

The material–air partitioning coefficient refers to  $K_{ma}$ , is the ratio of concentration in the material and air ( $K_{ma}=C_m/C_a$ ). According to the definition, increasing  $K_{ma}$  leads to movement of chemical to material side, whereas lower  $K_{ma}$  results in movement of which to air side.  $K_{ma}$  is calculated within temperature and  $K_{oa}$ : octanol–air partition coefficients. For PBDEs, the  $K_{ma}$  is nearly as an order of magnitude higher than  $K_{oa}$  (Waye, 2008), and  $K_{oa}$  value was obtained from references. Octanol–water partition coefficients and Henry's law constant are also used for calculating  $K_{oa}$  (Titlemier et al., 2001; Meylen and Howard, 2005). In this thesis,  $K_{oa}$  value refers to (Harner and Shoeib, 2002), by the correlation  $\log(K_{oa})=A+B/T$ , where  $T$  is the absolute temperature.  $K_{ma}$  is calculated by  $K_{oa}$  which displayed in Table 3-2.

Table 3-1. Octanol–air coefficient for BDE congeners(Tom Harner and Mahiba shoeib, 2002( $\log K_{oa}=A+B/T$ ))

PBDE congener	$\log K_{oa}$	A	B
47	10.53	-6.74	5068
100	11.13	-7.18	5459
99	11.31	-4.64	4757

Table 3-2. Material-air coefficient for BDE congeners

PBDE congener	logK <sub>oa</sub>	K <sub>ma</sub> (at 25cent i grade)
47	10.53	-6.74
100	11.13	-7.18
99	11.31	-4.64

## 2). Particle-air partitioning coefficient.

Many papers proposed that particle-air partition coefficient correlated to K<sub>oa</sub>. (Finizio et al., 1997) used twelve correlation to calculate K<sub>p</sub> and compare it to K<sub>oa</sub>. The result,  $\text{Log}(K_p) = \text{log}(K_{oa}) + \text{log}(\text{fom}) - 11.91$ , is most commonly used in literatures to obtain K<sub>p</sub>, where fom is the mass fraction of organic matter on the particles. While K<sub>oa</sub> is held constant and fom is varied.

The fraction of mass of organic matter available for adsorption on particles has been found to 0.19 to 1.0. fom Values for urban house dust smaller than 53 $\mu\text{m}$  and between 53–100 $\mu\text{m}$  are given as 0.27 and 0.204, respectively (Waye, 2008).

The EPA report has already shown the representative values of fraction of Vapor-particle phase for PBDE chemical, and three target compound in this study are displayed in table 3-3

Table 3-3: Vapor-Particle partitioning of PBDEs from reference(An Exposure Assessment of Polybrominated Diphenyl Ethers,2010)

Brominated diphenyl ether congener	Brominated diphenyl homologue	Vapor phase %	Particle phase %
BDE 47	tetraBDE	90	10
BDE 99	PentaBDE	61	39
BDE 100	PentaBDE	56	44

### 3). Henry's Law constant

Henry's Law constant(H) is an air-water partition coefficient, which is a measure of the chemical's equilibrium distribution between air and water at a specified temperature. Generally, H is derived from the ratio of vapor pressure to the chemical's aqueous solubility. Knowledge of H is essential to understanding the direction and mass flux of contaminants transferring from water to air (EPA, 2010). H is usually expressed as  $\text{Atm}\cdot\text{m}^3/\text{mol}$ . Chemicals with H values greater than  $10^{-3} \text{ atm}\cdot\text{m}^3/\text{mol}$  rapidly volatilize into air. For PBDEs, they are more settled chemicals with H at  $10^{-4} \text{ Atm}\cdot\text{m}^3/\text{mol}$  or less, and increasing bromination with lower degrees of H.



Table 3-4: Henry' s Law constant of PBDEs from reference

TARGET	Henry Law's constant(H)(atm-m <sup>3</sup> /mol at 25 centigrade)	Reference
BDE 47	$1.48 \times 10^{-5}$	ATSDR(2004)
	$8.39 \times 10^{-6}$	Centin et al.,(2004)
BDE 99	$2.27 \times 10^{-6}$	ATSDR(2004)
	$5.92 \times 10^{-6}$	Centin et al.,(2004)
BDE 100	$6.81 \times 10^{-7}$	ATSDR(2004)
	$2.37 \times 10^{-6}$	Centin et al.,(2004)

#### 4). Vapor pressure

Volatilization of a chemical and its presence in air is depends on Vapor pressure of the chemical. Vapor pressure also determines the particle-vapor phase distribution in air of PBDEs. Vapor pressure is defined as the force per unit area from a chemical in vapor phase while in equilibrium with its liquid or solid phase at a specified temperature. For PBDEs, Vapor pressure is usually in units of Pascal (Pa) or millimeter of Hg(mmHG). Generally, volatile organic compounds have a solid phase that higher than 10Pa at 25 centigrade in air (Olsen and Nielsen, 2001). The semivolatile organic compounds tend to have

solid phase vapor pressure lower than 1 pa at 25 centigrade. Since that PBDEs are semivolatile organic compounds. Lower degrees of Bromianation of PBDEs usually have higher vapor pressure. Table 3-5 shows that vapor pressure value which from different literatures, for this study, the values from (Tittlemier et al., 2002) are used for calculation.

Table 3-5 vapor pressure of target BDE congeners from reference

TARGET	Vapor pressure(Pa)	Reference
BDE 47	0.000186	Tittlemier et al.,(2002)
	0.000215	Wnaia et al., (2002)
	0.000250	Wong et al.,(2001)
BDE 99	0.0000176	Tittlemier et al.,(2002)
	0.0000363	Wnaia et al., (2002)
	0.0000682	Wong et al., (2001)
BDE 100	0.0000286	Tittlemier et al., (2002)
	0.0000368	Wnaia et al., (2002)

## 2. PBDEs concentration

### (1) outdoor concentration

Outdoor concentration of BDE 47, 99, 100 are refers to ME, Korea, 2009, which is the data related to ventilation process and air exchange process in IIAQ model.

As figure 3-1 indicated, Beside BDE 209; BDE 47, BDE99 and BDE 100 are the second highest group among all monitored congeners, which are similar to the situation of indoor PBDEs. Value of PBDEs are the average value nationwide.

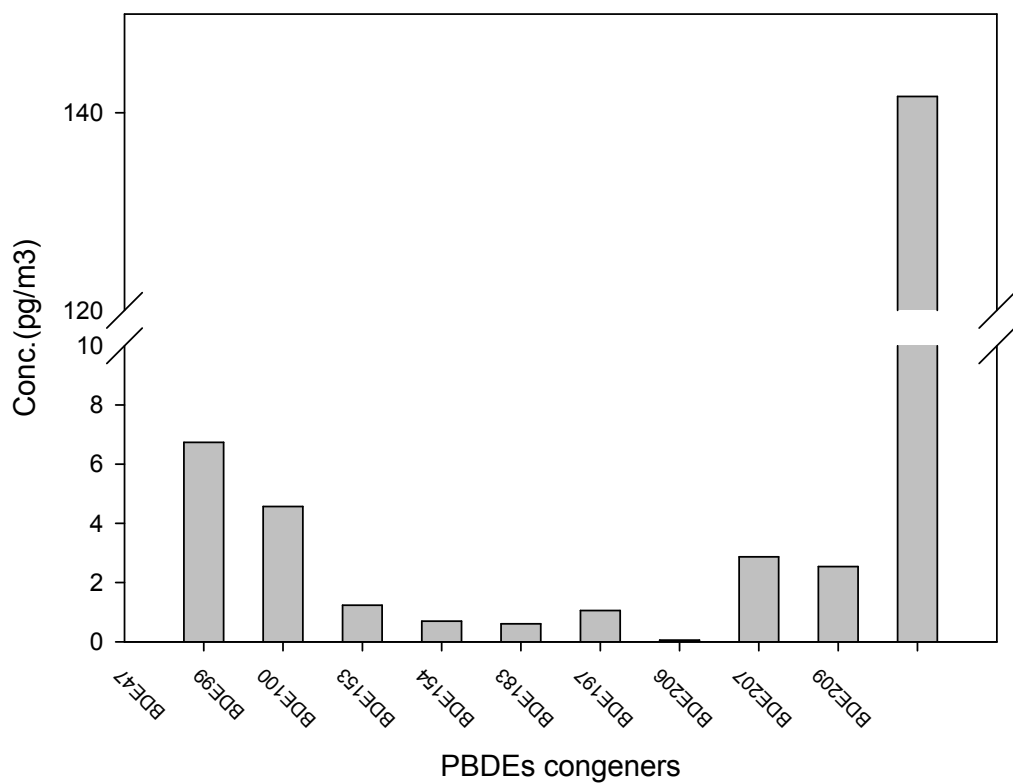


Figure 3-1, PBDE outdoor concentration in south Korea by congeners(Me, 2008, 2009)

(2) Indoor PBDEs concentration(air)

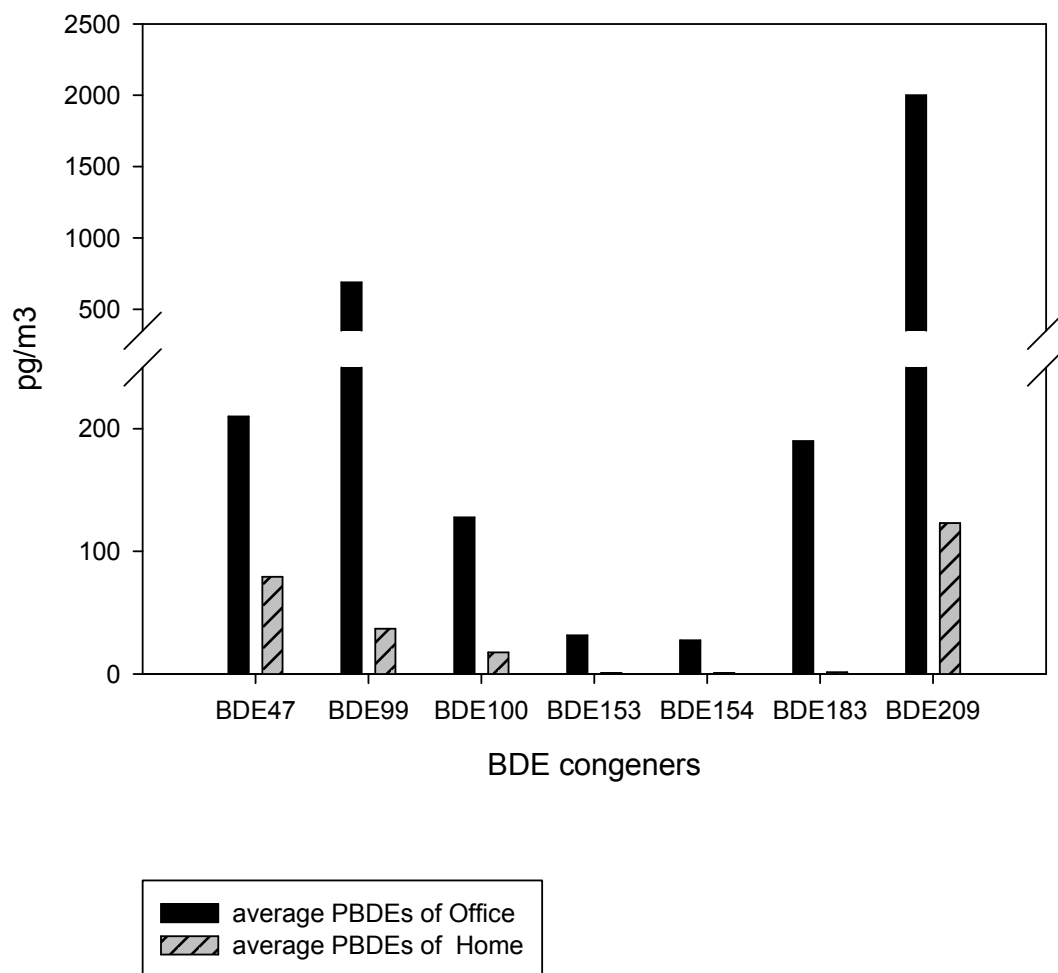


Figure 3-2. Comparison of PBDEs concentration in vapor phase (Vorkmap, 2010; Toms et al., 2009, Thuresson et al., 2011.; Wijesekera, 2004)

As figure 3-2 indicated (Vorkmap, 2010; Toms et al., 2009; Thuresson et al., 2011; Wijesekera, 2004), Concentration pattern of BDE congeners in indoor environment is similar to which in outdoor environment. The most highest group in concentration are BDE 47, BDE 99 and BDE 100 except BDE 209. The concentration of BDE 99 is the highest one among the three in office, whereas BDE 47 is dominated in home among the three.

Comparing the PBDE congeners both in office and home, it is found that, the concentration of PBDEs in office are obviously higher than which in home. The reason may relate to the Frequently use of computer in office than in home,

### 3. Indoor environment

#### (1) Space information

Table 3-6 basic information of 3 different indoor environment

<b>Apartment</b>	<b>value</b>	<b>Reference</b>
Room-size(m2)	92.94	Statistics Korea
Furniture surface(m2)	20.75	Internet information
Computer number(#)	1~2	Ki-Chul,Sung and Chung-Yoon,Chun, 2005
Interior material -related	-	
<b>Research Office</b>		
Room-size(m2)	(28~72)*3	Query
Furniture surface(m2)	10.61m2	Query
Computer number(#)	2~15	Query
Interior material -related	-	
<b>Internet café</b>		
Room-size(m2)	145~160	Ki-Chul,Sung and Chung-Yoon,Chun, 2005
Furniture surface(m2)	44.62	Query
Computer number(#)	47~66	Ki-Chul,Sung and Chung-Yoon,Chun, 2005
Interior material -related		

The information collected from literature and other ways of three different indoor environment are shown in table 3-6; The space of internet cafe is the largest one among the 3 indoor environment, and the density of computer in indoor space is the highest as well. In contrast, the common home has the smallest size among the three spaces, but the density of computer is the lowest as well.

However, when people using computer, they may use the computer in a single

room. So, in most of the time, the danger from computer will appear in the single room that computer is operating. Sometimes people use the computer with opening door and windows, whereas sometimes they close the door and windows, which indicate different scenario of natural ventilation.

In most of research office, the size of research office are similar than other 2 spaces, which is around  $50m^2$ , and the number of computers is ranged from 2 to 15; In this study, it is only focus on the science research office in this study. In addition, it is assumed that mechanical ventilation operated within work time.

Little information about the internet cafe in south Korea has been found, most of which concerns about the PM concentration and its harmfulness to people in the place. As shows in table 3-6 the computer density in internet cafe is the highest among the three places. So it is predicable that, PBDEs will appear in higher concentration in where. In addition, one point that need to concentrated on is that ACH rate is low in most of internet cafe and the particle concentration is higher than other indoor environment, with the reason that PBDEs incline to bound to particles, the concentration of PBDEs will be high by the combined reason.

## **(2) Furniture information**

furniture is also very important for simulation, since that different indoor environment usually has different furniture pattern depends on their functions. And, Larger surface of furniture always indicate larger deposition surface. Both furniture information about home and internet cafe are collected from internet (table 3-7). Due to the reason that only one room of a house will be tested in this study, double bed, one desk and two small drawer set have been considered for the standard simulation condition in a typical room in a house. The furniture used in internet cafe are similar. Therefore, a typical type of furniture information are applied in this study for internet cafe. A survey was conducted for information of research room collection, the target are the students who are studying in research rooms in Seoul National University (table 3-8).

Table 3-7. Surface area of furniture,(internet information)

Furniture	value	reference
Single bed	1,100mm(Width)x2,000 (Length)	<a href="http://kin.naver.com/qna/detail.nhn?d1id=13&amp;dirId=13050501&amp;docId=38441579&amp;q=7Lmo64yA6rec6rKp&amp;enc=utf8&amp;section=kin&amp;rank=2&amp;search_sort=0&amp;spq=1">http://kin.naver.com/qna/detail.nhn?d1id=13&amp;dirId=13050501&amp;docId=38441579&amp;q=7Lmo64yA6rec6rKp&amp;enc=utf8&amp;section=kin&amp;rank=2&amp;search_sort=0&amp;spq=1</a>
Double bed	1,500mm(Width)x2,000 (Length)	<a href="http://kin.naver.com/qna/detail.nhn?d1id=13&amp;dirId=13050501&amp;docId=38441579&amp;q=7Lmo64yA6rec6rKp&amp;enc=utf8&amp;section=kin&amp;rank=2&amp;search_sort=0&amp;spq=1">http://kin.naver.com/qna/detail.nhn?d1id=13&amp;dirId=13050501&amp;docId=38441579&amp;q=7Lmo64yA6rec6rKp&amp;enc=utf8&amp;section=kin&amp;rank=2&amp;search_sort=0&amp;spq=1</a>
Desk	1600mm(Width)x1200 mm(Length)x720mm (Height)	<a href="http://cafe.naver.com/ggprice/893">http://cafe.naver.com/ggprice/893</a>
Desk	1600mm(Width)x1200 mm(Length)x720mm(H eight)	<a href="http://cafe.naver.com/ggprice/893">http://cafe.naver.com/ggprice/893</a>
Small drawer set	400mm(Width)x510mm (Length)x600mm (Height)	<a href="http://cafe.naver.com/ggprice/893">http://cafe.naver.com/ggprice/893</a>
Desk	1600mm(Width)x1200 mm(d)x720mm(Height)	<a href="http://cafe.naver.com/ggprice/893">http://cafe.naver.com/ggprice/893</a>
Sofa	1750(Length)x990(Widt h)x980(Height)	<a href="http://cafe.naver.com/hyuplus2010/4344">http://cafe.naver.com/hyuplus2010/4344</a>



Table 3-8. result of survey from the students of seoul national university, 2012. 5

Name	Department	Size (m2)	height (m)	Number of computer	Desk-upward surface(m2)	Desk-side surface (m2)	Shelf (upward; m2)	Shelf (side surface)
QuanXiaoWen	Biology	50	3	12	1	1	1.5	0.5
YinHe	Environmental planning	28	3	8	1	1	1.5	0.5
Zhongxiancai	Medical Science	32	3	10	1	1	1.5	0.5
Zhang Yao	Physical Science	40	3	5	1	1	1.5	0.5
Chen yu	-	60	3	6	1	1	1.5	0.5
WangLiang	astronomy	35	3	7	1	1	1.5	0.5
Liu Hai	Chemistry	40	3	10	1	1	1.5	0.5
Zheng Ling	-	52	3	10	1	1	1.5	0.5
Chen Xi	-	36	3	6	1	1	1.5	0.5
Zhang qiankun	Computer Science	54	3	15	1	1	1.5	0.5
Li yiming	-	60	3	9	1	1	1.5	0.5
Lee ki-en	-	40	3	4	1	1	1.5	0.5
Kim kyung-ho	-	60	3	13	1	1	1.5	0.5
Cha zunyor	-	72	3	10	1	1	1.5	0.5
Zhao peng	-	40	3	2	1	1	1.5	0.5
Ma Chao	-	35	3	8	1	1	1.5	0.5
Wu Di	-	54	3	9	1	1	1.5	0.5
Li yunbo	-	28	3	5	1	1	1.5	0.5
Xie han	-	48	3	10	1	1	1.5	0.5

## **4. Model modification**

In this study, IIAQ model is used for simulation. However, refers to (Won & Lee, 2007) this model is mainly applied for VOCs, PBCs and PAHs, thus certain variation should be carried out to apply for PBDEs

### **1. Emission rate**

According to the figure 2-1, it is known that in previous IIAQ model, the compartment is divided to air compartment and material compartment. The main emission sources is considered as material compartment and other emission source. However, in this thesis, PBDEs are thought as mainly from electrical appliance in indoor environment, which is personal desktop computer. Due to the reason, computer panel is set as the only emission source in the overall indoor space. Since PBDEs are released from volatilization process (EPA, 2010), the emission rates of PBDEs congeners are correlated to temperature in indoor environment.

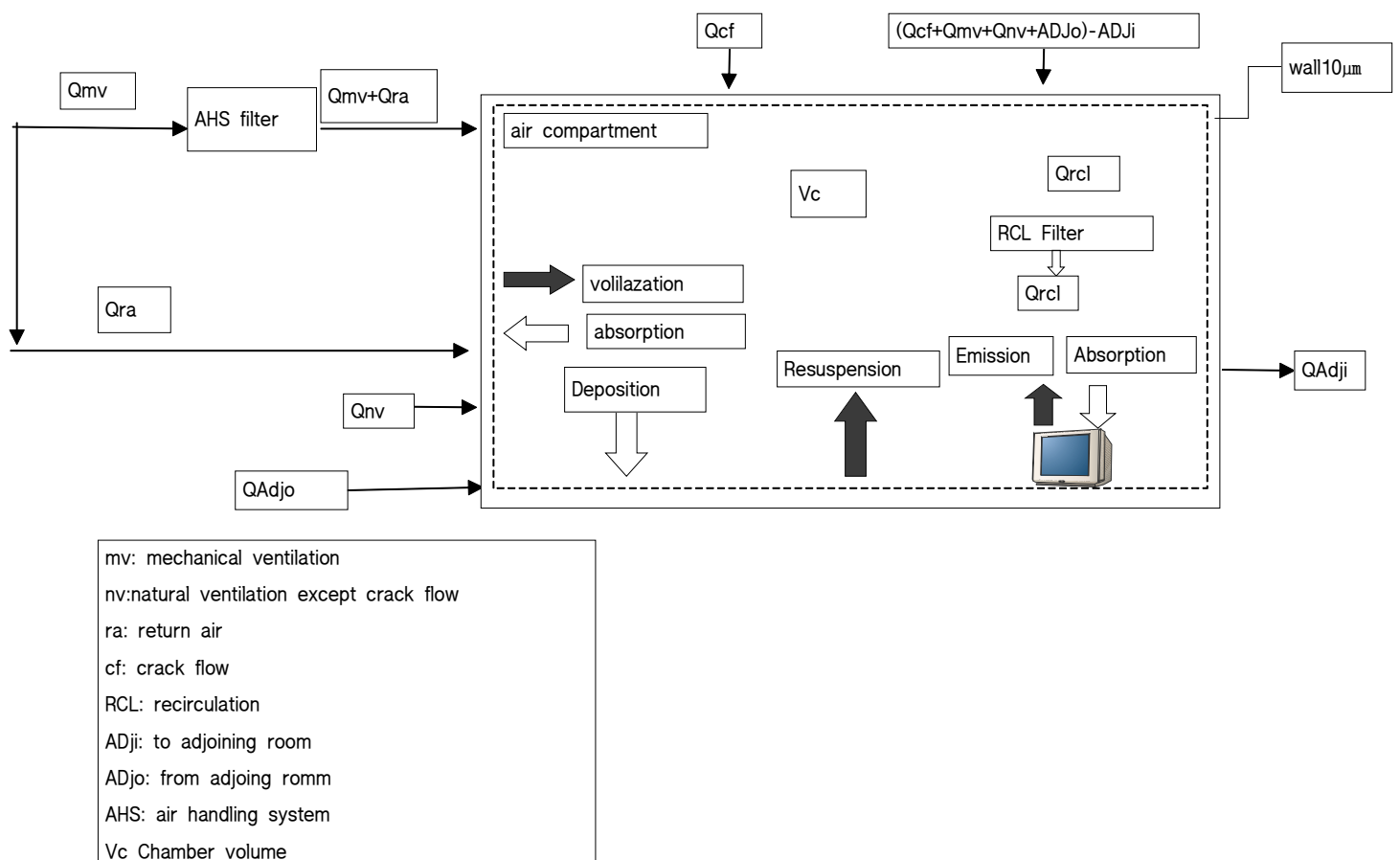


Figure 4-1. Conception of modified Integrated Indoor air quality model

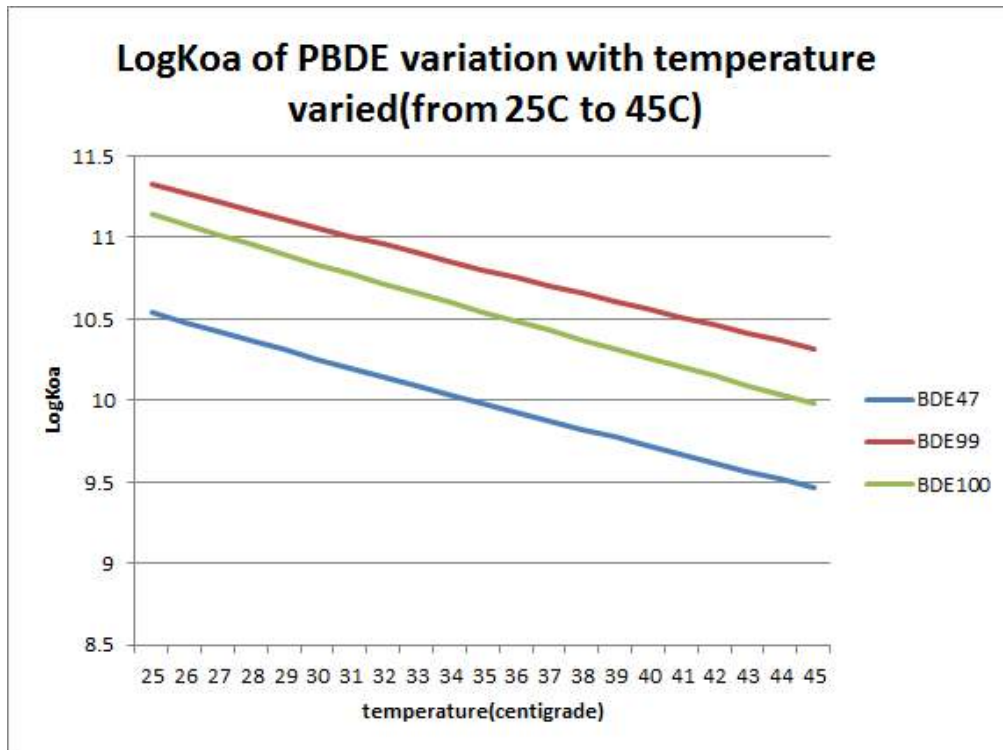


Figure 4-2. LogKoa calculation by temperature.

Material-air coefficient ( $K_{ma}$ ) is about 10 times of Octanol-air ( $K_{oa}$ ) coefficient (Waye, 2008). As the temperature increases, the value of LogKoa decrease and higher bromination leads to higher values of logKoa (Figure 4-2). The Values of  $K_{ma}$  can be obtained from  $K_{oa}$  values.

$$K_{ma} = K_{oa} \times 10$$

And since the Mass transfer coefficient from air side ( $MTC_{air}$ ), is calculated in IIAQ model by the equation

$$MTC_{air} = sh \times (\text{diffusivity}_{air} / \text{slab surface}^2)$$

where:

MTC: Mass transfer coefficient from air side  
diffusivity<sub>air</sub>: diffusivity of PBDEs in indoor air  
Slab surface: the surface of computer slab which releases PBDEs

By calculated values of K<sub>ma</sub> and MTC<sub>air</sub>, The flux of air to slab and slab to air is available by the equation that

$$\text{Flux}_{\text{air}} = \text{MTC}_{\text{air}} \times C_{\text{slab}} / K_{\text{ma}} \times \text{Slab surface}$$

$$\text{Flux}_{\text{slab}} = \text{MTC}_{\text{air}} \times C_{\text{air}} \times \text{Slab surface}$$

Where

Flux<sub>air</sub>: the volatilization rate of PBDEs from slab to air (g/sec)  
Flux<sub>slab</sub>: the absorption rate of PBDEs from air to slab  
C<sub>slab</sub>: the concentration of PBDEs in the computer slab(g/cm<sup>3</sup>)  
C<sub>air</sub>: the concentration of PBDEs in air side(g/m<sup>3</sup>)

The difference of the volatilization rate of PBDEs from slab to air and absorption rate of PBDEs from air to slab is identified as the emission rate from the computer for this study. Hence, emission rate will be varied with the temperature changed. which is more accurate method than given a constant emission rate in previous IIAQ model. And, it is also possible that differentiate the situation that computer on and off.

$$\text{Emission rate} = \text{Flux}_{\text{air}} - \text{Flux}_{\text{slab}}$$

## 2. Vapor pressure and air-particle partitioning coefficient.

The partitioning of semivolatile organic compounds in air is an very important factor for their fate and transport both in indoor and outdoor space. According to (Goel et al., 2006), the vapor-particle partitioning coefficient of PBDEs are depend on sub-cooled liquid vapor pressure( $P^{oi}$ ), which are not reflected by previous IIAQ model. Thus  $P^{oi}$  are calculated as

$$\log P_L^o = \frac{A}{T} + B$$

which A and B are constants(BDE-47,A=-4872.5, B=12.74; BDE99, A=-5435.5, B=13.77; BDE100, A=-5339, B=13.37; reference: Goel et al., 2006). Therefore ,the vapor-particle partition coefficient are described by the linear relationship:

$$\log K_p = m_r \log P_L^o + b_r$$

where  $m_r$  and  $b_r$  are constants as well calculated from (Goel et al., 2006; BDE 47  $m_r=-0.9755$ ,  $b_r=6.9501$ ; BDE 99  $m_r=-0.7812$   $b_r=6.1337$ ; BDE100  $m_r=-0.9592$ ,  $b_r=7.142$ ).

### **3. Wall Compartment**

Instead of material compartment, the wall compartment is inserted to the model. The wall covered the overall compartment of indoor space. The initial concentration of PBDEs in the wall is considered as “0”, with time varied, PBDEs in indoor air absorbs by the wall; Wall also releases PBDEs to air.

### **4. Outdoor PBDEs**

In previous IIAQ model, the PBDEs concentration in outdoor atmosphere was constant. However, in real world, many factors impose impact to outdoor concentration of PBDEs, such as temperature and Total suspended particle (TSP) concentration. Thus, this part is designed as a variable part, the concentration of outdoor PBDEs can be designated in certain period of time. However, no representative value of outdoor PBDEs concentration by time period has been reviewed. This function has not been applied in following study.

### **5. Air exchange**

Air exchange is an significant part in predication, since that frequently air exchange result in lower concentration of chemical in indoor space.

In modified IIAQ model, the air exchange period of time can be designated during 24 hours per day. For example, many Korean family incline to clean the house and exchange air between 10:00 and 11:00 am.

Therefore, It is possible that invistigate when is the optimum time to clean the indoor space or exchange air in order to minimize the possibility of PBDEs exposure to human.



## 5. model evaluation

### (1)BDE 47

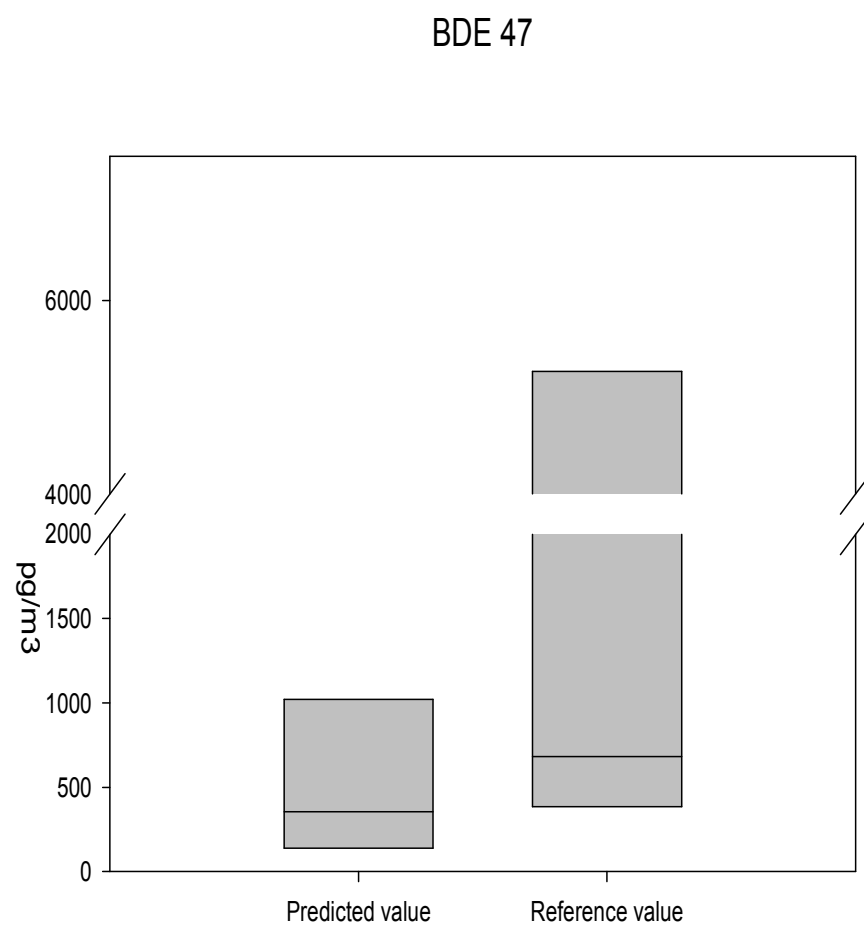


Figure 5-1 Compare of Predicted value and reference value of BDE 47

(2)BDE 99

BDE 99

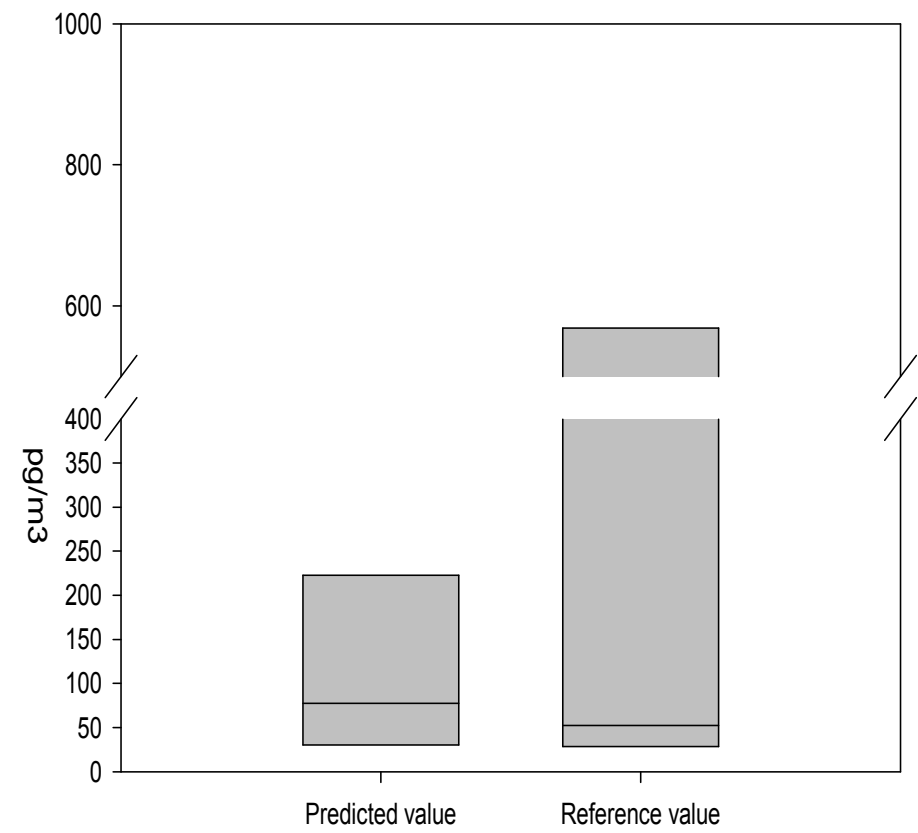


Figure 5-2 :Compare of Predicted value and reference value of BDE 99

(3)BDE 100

BDE 100

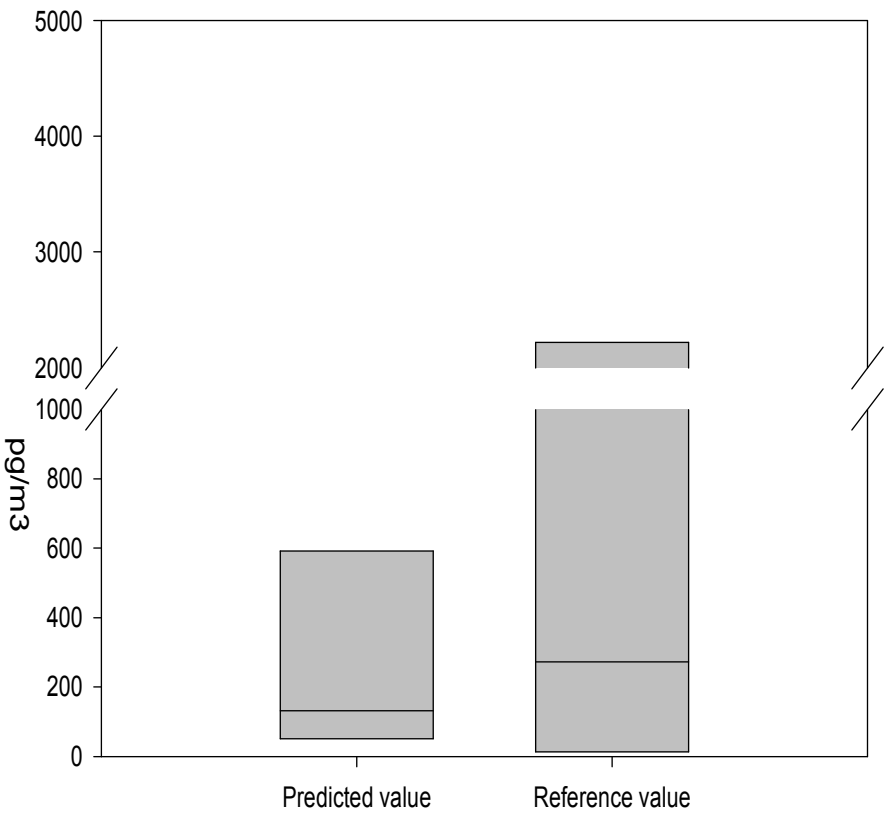


Figure 5-3: Compare of Predicted value and reference value of BDE 100

Table 5-1 Measured value from reference

Evaluation Reference information							
Chemical		computer #	BDE47 concentration (pg/m <sup>3</sup> )	BDE99	BDE100	Filter-related information	Reference
Vapor phase		2	1360	73	157	none	Harrad et.al 2004. (Preliminary Assessment of U.K. Human Dietary and Inhalation Exposure to Polybrominated Diphenyl Ethers)
		16	7140	1450	6510	none	
		12	4640	275	789	none	
		1	770	145	465	none	
		6	497	53	9	none	
		2	645	37	80	none	
		2	1330	82	209	none	
		1	721	52	133	none	
		3	45	3.7	13	none	

Since that no much reference contains the indoor space information which reports monitoring data of PBDE congeners, only the paper from Harrad et.al 2004 has been used for estimation for IIAQ model.

Concentration of BDE 47, BDE99, BDE100 are calculated by modified IIAQ model respectively within computer number of 1, 2, 3, 6, 12, 16. The result shows in figure 5-1, 5-2, 5-3. compare to the observed value. It is known that the average value of both simulated value and observed value are similar to

each other. However, observed value shows huge differences with each other. It may be because of ventilation situation and different use of land.

## 6. Results and Discussion

since that computer is not always operating in real world, it is necessary to divide the situation into time range of computer on and time range of computer off. The increase of internal temperature of desktop computer indicates that the emission rate of BDE 47, BDE 99 and BDE 100 will be increased constantly as well until the temperature become 45 centigrade, and then emission rate of computer will be constant when computer is on. And after the computer off, the emission rate will decrease again, and keep a constant emission rate in 25 centigrade. In this study, it is assumed that the temperature increase from 25 centigrade to 45 centigrade in one hour.

The simulation is conducted under following assumption.

For home, it is considered that after work, people will go home have a rest and surf the internet for about 4 hours, and the time is considered from 19:00 to 23:00.

For research office in university, most of students and researchers go for work from 9:00 until 5:00, typically 8 hours.

For internet cafe, since the computer is always on in 24 hours, so the temperature of every computer will be constant and the emission rate will be a constant value.

## 1. .particle size distribution

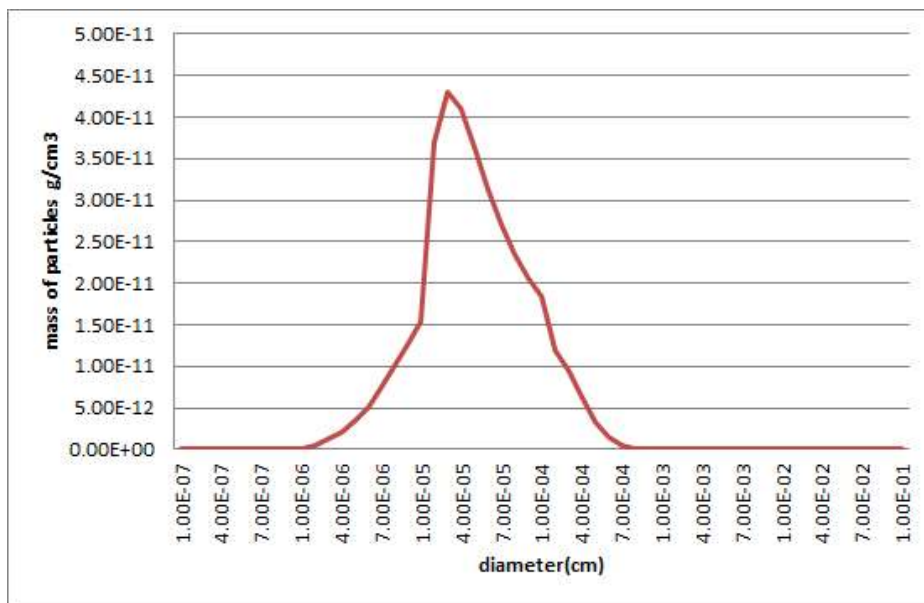


Figure 6-1 modeled indoor chemical mass distribution from home

figure 6-1 shows that mass distribution. It is known from figures that the high concentration of particles lumped in  $0.01\mu\text{m}$  to  $10\mu\text{m}$ , thus, the particles in this range have the dominant surface size compare to other particles with other diameter range, which means that more spaces are available for PBDEs. Hence, more existing small size particles result in high risk of exposure to people who lives in such a indoor environment.

The chemical concentration of PBDEs which adsorbed to particles divided by size is also calculated, which indicated that more than 99,8% PBDEs is absorbed to

the particle which the diameter less than  $1\mu\text{m}$ , whereas only 0.02% PBDEs is absorbed to the particles within  $1\mu\text{m}$  to  $10\mu\text{m}$ .

## **2. flux analysis**

In order to understand how the processes effects on each other, a general scenario is selected for flux analysis. The scenario is assumed as a single room with one computer exist which are using for 4hours (19:00 to 22:00) and the outdoor concentration varied by the time of period which indicated in model modification part above, and people who live in such a space open the windows when using the computer equipment.

### **1). Concentration variation pattern**

The concentration results are displayed in figure 6-3, which are particle phase and vapor phase respectively. The result are simulated with 1 hour resolution, and 24 hour geometric mean of the value has been used for checking how concentration of BDE 47 varied in indoor environment. The initial concentration was set as "0". The concentration increase slightly with a constant rate. Thus, the BDE 47 concentration reaches steady status as soon as simulation start.

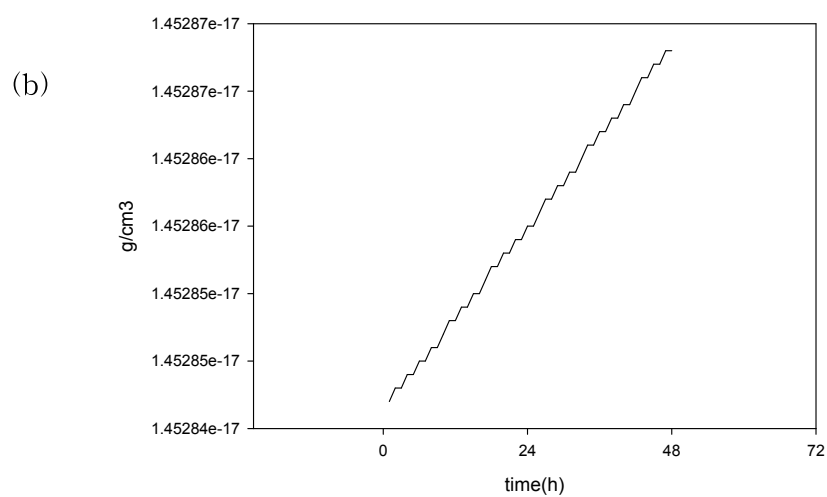
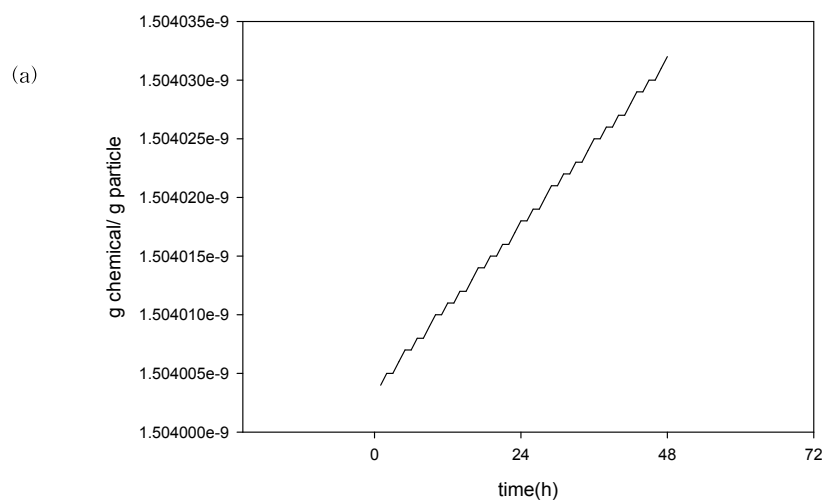


Figure 6-3.(a) Particle phase BDE 47 concentration variation within 3days  
 (b) Vapor phase BDE 47 concentration variation within 3days



## 2). Emission

The emission flux was calculated by the one hour scale, and refers the scheme of modified IIAQ model, it is known that the emission rate of indoor system is the difference of volatilization from slab (figure 6-3(a)) and absorption to the computer slab (figure 6-3(b)).

Obviously, comparing to the volatilization from slab, the absorption to computer slab is much smaller, thus, the emission rate of PBDEs are considered dominated by the volatilization from computer slab. Since the modified IIAQ model set the emission rate as a function of temperature (computer on and off).

Figure. 6-3 shows that the emission rate of computer slab is reflecting the variation of temperate. At 18:00 to 22:00 every day, operating computer result in 1070% higher emission of BDE 47 than which of computer in off status, which is close to the result (911% higher) from (Waye, 2008)

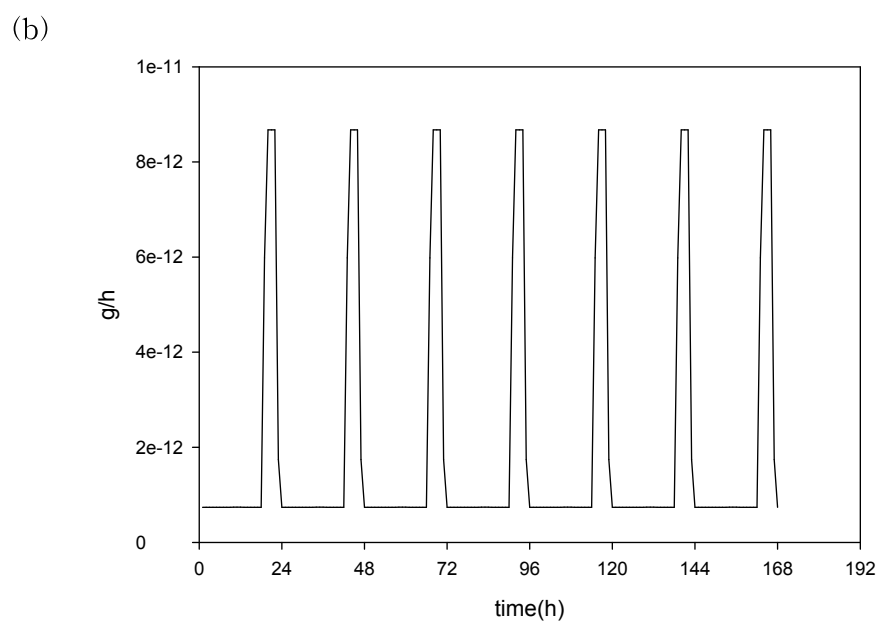
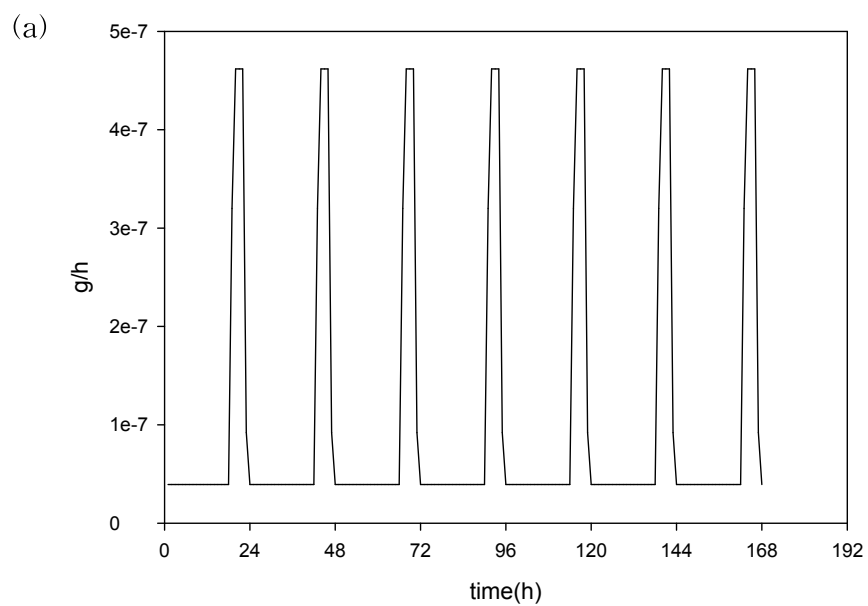


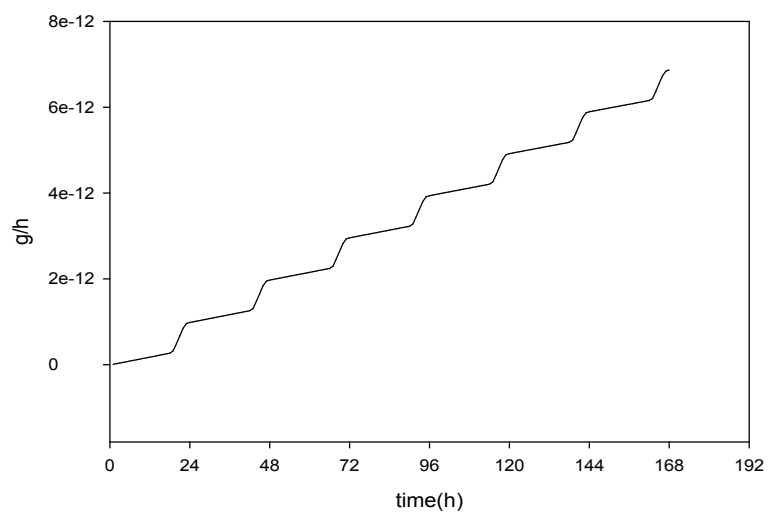
Figure 6-4: (a) volatilization flux from computer slab  
(b) Absorption flux to computer slab

### **3). Wall compartment**

The wall is considered as a material with 10nm thickness with initial BDE 47 concentration of “0”.

As figure 6-8 shows, the flux of BDE 47 to the wall has the similar pattern with emission flux, which indicates that at 18:00 to 22:00 the flux to the wall is highest combined with using computer. However, for the process of volatilization from the wall. For the reason that the remain BDE 47 in the wall accumulated, the more BDE 47 accumulation in the wall result in higher volatilization rate to the air side in indoor space.

(a)



(b)

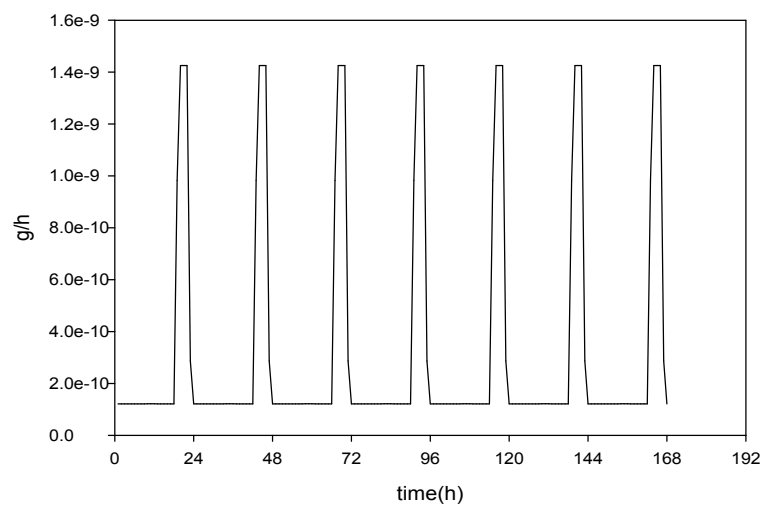
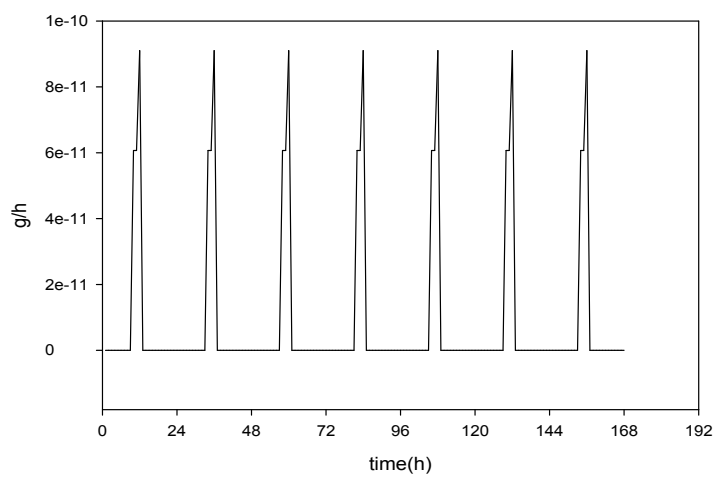


Figure 6-5. (a) BDE 47 flux from wall  
(b) BDE 47 flux to wall

#### 4). Natural ventilation and Air Exchange

Natural ventilation means that, once door or windows in the system opens, the inflow of outdoor PBDEs, which shows in the figure 6-6(a). For the reason that, 18:00 to 22:00 are also set as the time of period for ventilation. Thus, it is understood that the flux from outdoor atmosphere is highest at 18:00 to 22:00. Air exchange refers to the chemical outflow to atmosphere while the door and windows open (Figure 6-6). Compare to figure 6-6(a) and 6-6(b), it is found that, the natural ventilation inflow is slightly higher than outflow through the air exchange process, Therefore, the chemical concentration which refers to BDE 47 in this study in indoor air probably increase during the ventilation process, because of low level BDE 47 concentration in indoor space.

(a)



(b)

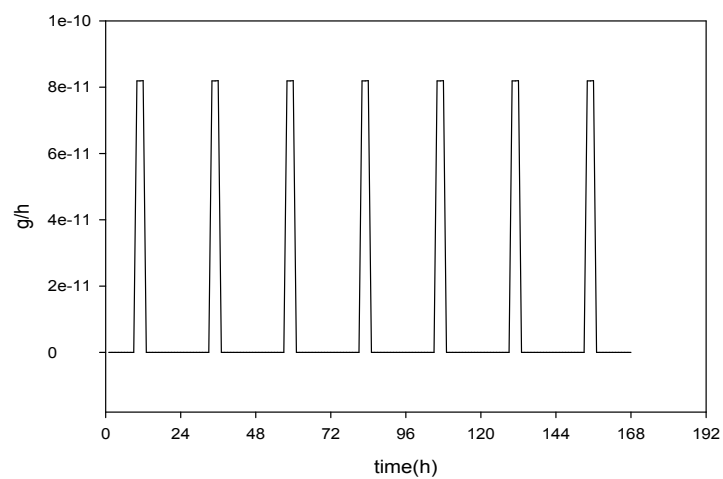


Figure 6-6. (a) Natural ventilation flux of BDE 47  
(b) Air exchange flux of BDE 47

## 5). Deposition

Refers to figure 6-7, Initial flux through deposition is high and decreased continuously until computer is operated, because of the TSP concentration in air is decreased with time due to deposition process. However, while computer is operated with ventilation, the chemical concentration in air surges while the particles in outdoor air inflow to indoor environment (TSP in outdoor air is calculated as  $95\mu\text{g}/\text{m}^3$ , whereas TSP in indoor environment is calculated as  $30\mu\text{g}/\text{m}^3$  ).

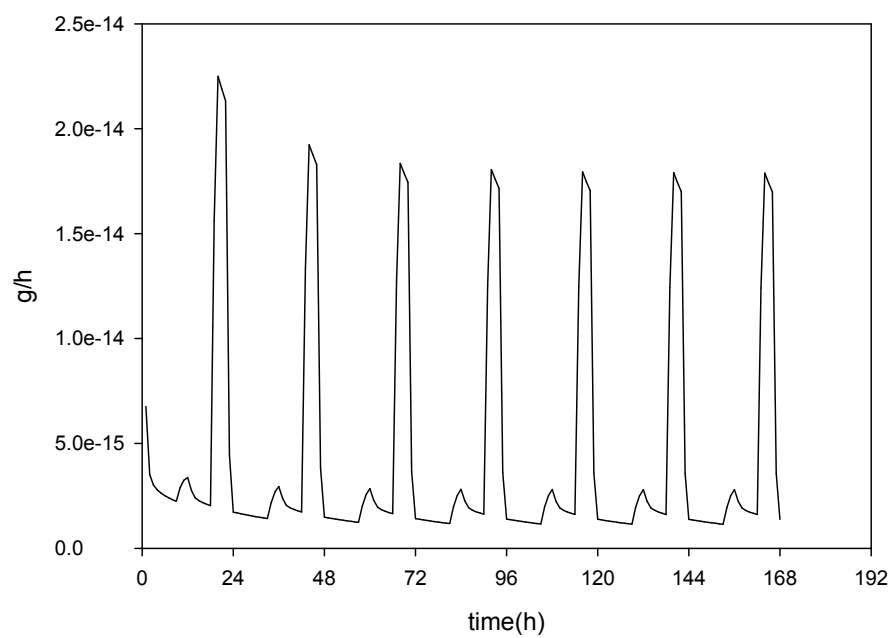


Figure 6-7. Deposition flux of BDE 47



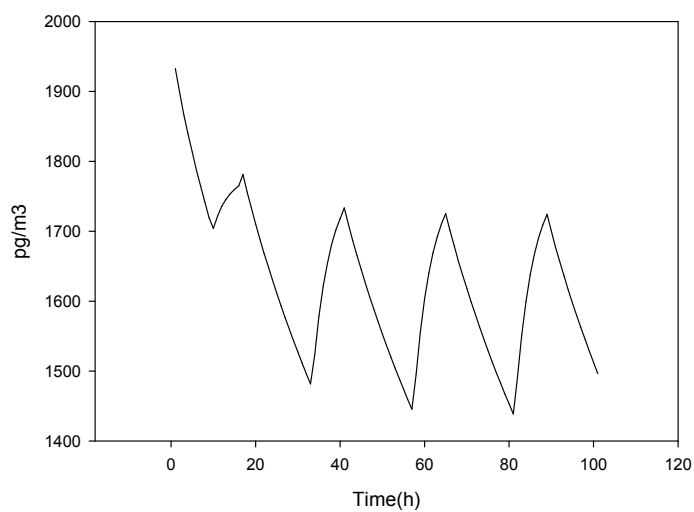
### 3, Ventilation effect

This scenario set so as to understand how the ventilation process impacts on the situation with using computer and computer off, respectively.

Because, in general situation, the BDE 47 concentration in outdoor is in the similar level with which in indoor environment. Thus, the effect of ventilation is not such obvious. The average value of prediction is 170.30 pg/m<sup>3</sup> with ventilation and 170.52pg/m<sup>3</sup> without ventilation respectively.

Therefore, the emission rate has been 10 times so as to explore the effect of ventilation, and the computer are always operating and off respectively. According to Figure 6-8, the concentration of BDE 47 is decreased sharply during the ventilation period (21:00 to 9:00), comparing to non-ventilation period, the concentration level of BDE 47 decreased 11.3% by ventilation process both when computer on and off, which proves that ventilation process would be a significant method to decrease the risk of PBDE exposure to human.

(a)



(b)

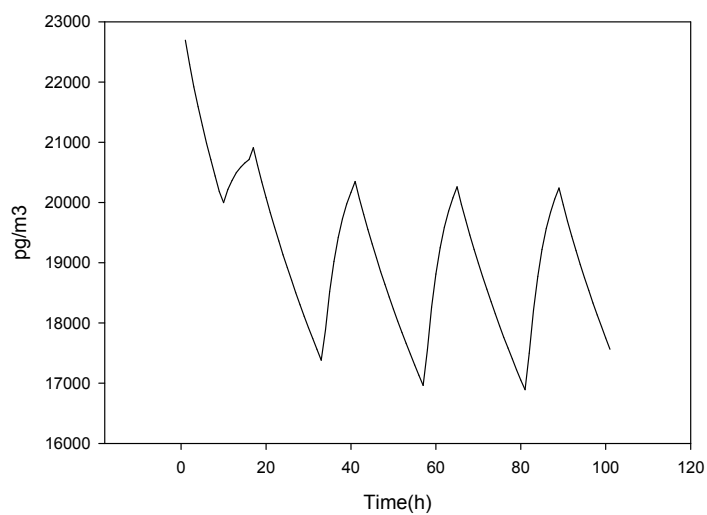


Figure 6-8. (a) BDE47 concentration with Computer off and ventilation  
(b) BDE47 concentration with Operating computer and ventilation

#### 4. Effect of operating computer

Because that computer is the most important emission source in assumed indoor environment. It is necessary to understand how an operating computer affect the PBDE chemical in indoor space.

The assumption is that one computer in a single room of the house, thus how the concentration of BDE 47 varied by operating the computer.

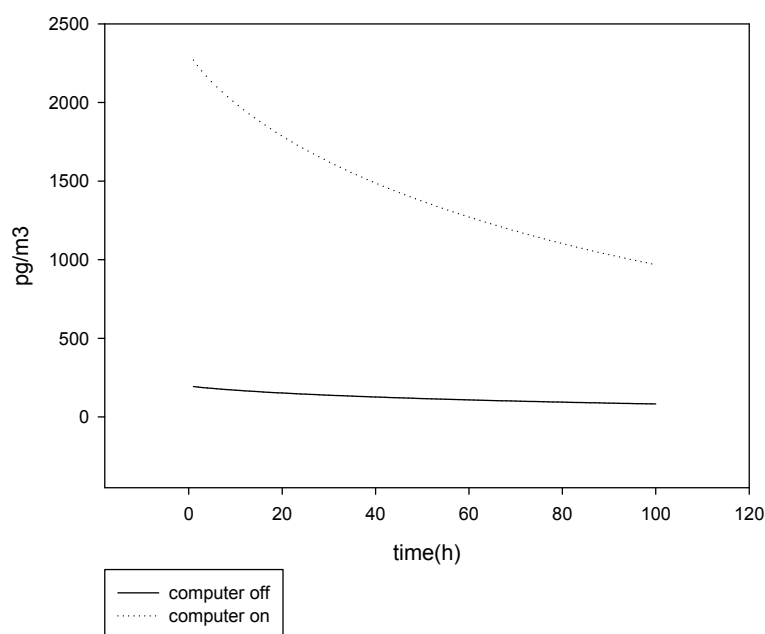


Figure 6-9. BDE 47 concentration with computer operating and off

The average of BDE 47 concentration when computer operating is 1397pg/m<sup>3</sup> and 119 pg/m<sup>3</sup> when computer is off, it is obviously that use of computer would lead to more risk for human exposure to PBDEs.

## 5. Temperature in indoor environment

It is also curious that how concentration of PBDEs varied within indoor temperature variation. From 10 centigrade to 40 centigrade, the simulation is conducted by every 5 centigrade, and the outcome is shown by figure 6-10, Apparently, even that change is sight, there is a reverse relationship between indoor temperature and BDE 47 concentration.

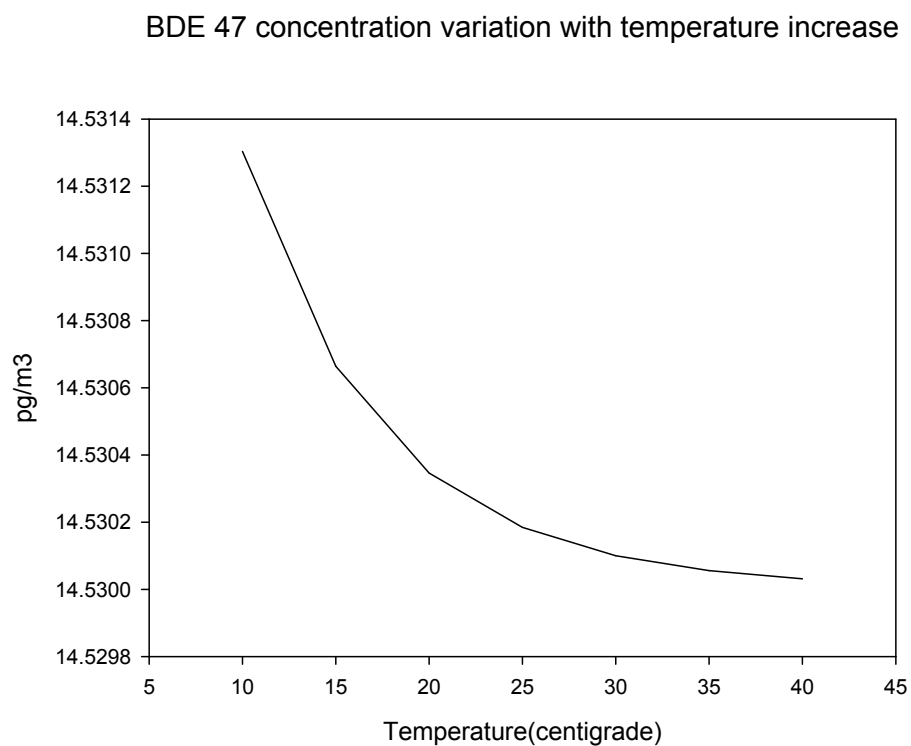


Figure 6-10. indoor temperature effect on BDE 47 concentration

6. Outdoor concentration

The BDE 47 concentration in atmosphere is also possibly impose effect on indoor BDE 47 concentration. In order to understand how outdoor BDE 47 concentration affect indoor environment, several outdoor BDE 47 concentration has been assumed, which are 1 time, 10 times, 100 times, 1000 times and 10000times of a given value separately. The result shows in figure 6-11, between 1 time to 100times, the impact on indoor concentration is not such apparent. However, from the range of 100 times to 10000 times, huge impact on indoor BDE 47 concentration can be discovered. In this study, the outdoor BDE 47 concentration in urban area is applied. But, in industrial area, the BDE 47 concentration in atmosphere is several hundreds times of which in urban area. It

BDE 47 concentration varied with outdoor concentration

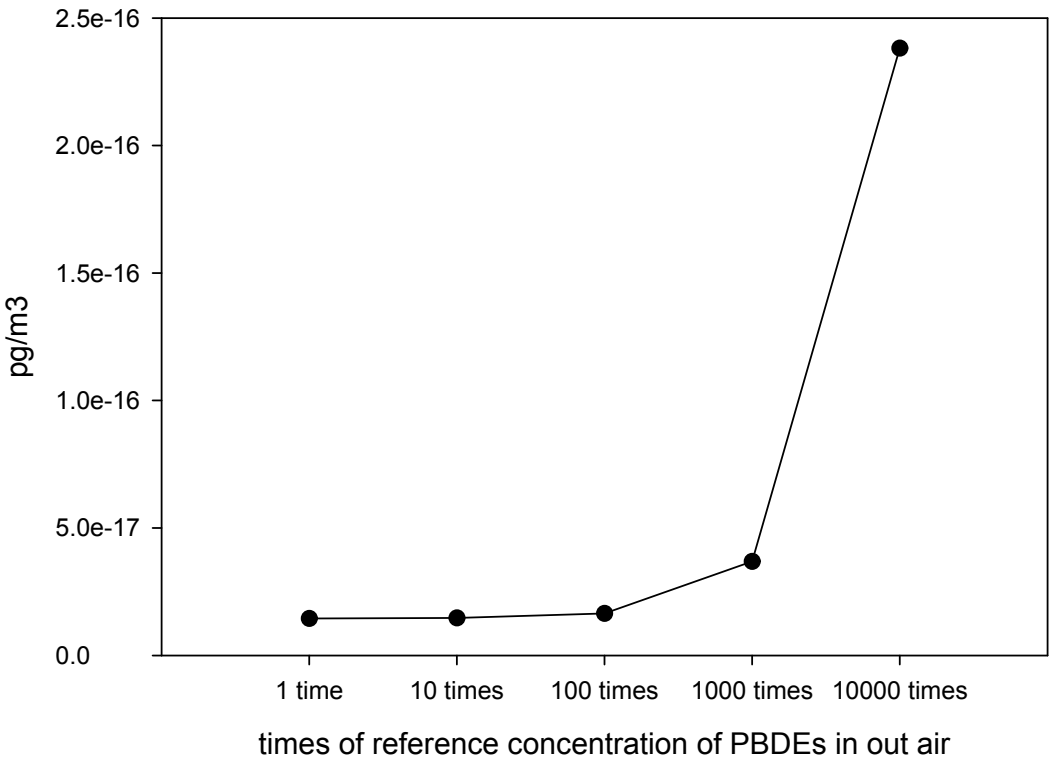


Figure 6-11. Outdoor BDE 47 concentration affect the indoor BDE 47 concentration

may cause high risk of exposure to people live in industrial area.

Table 7-1. simulation condition for South Korea

Type	Height (m)	surface size (m <sup>2</sup> )	Computer (#)	time of period using computer	Ventilation time
Home	3	5*3	1	19:00~22:00	10:00~12:00
Research office	3	9*5	10	9:00~17:00	6:00~19:00
Internet café	3	15*10	55	0:00~24:00	0:00~24:00

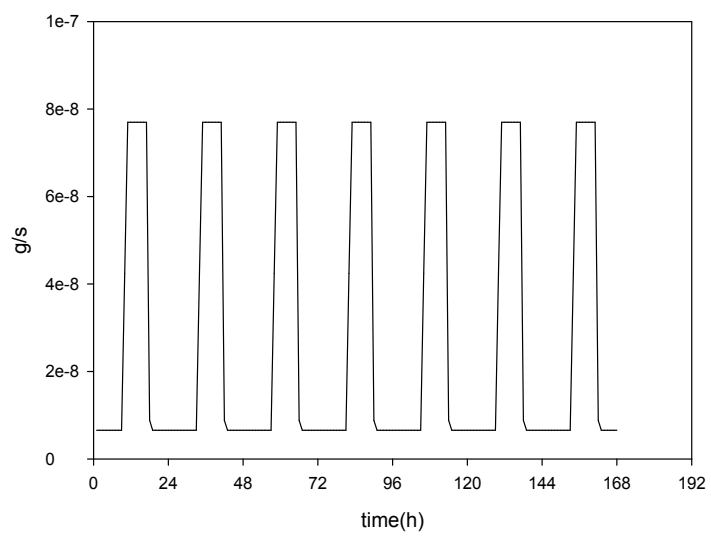
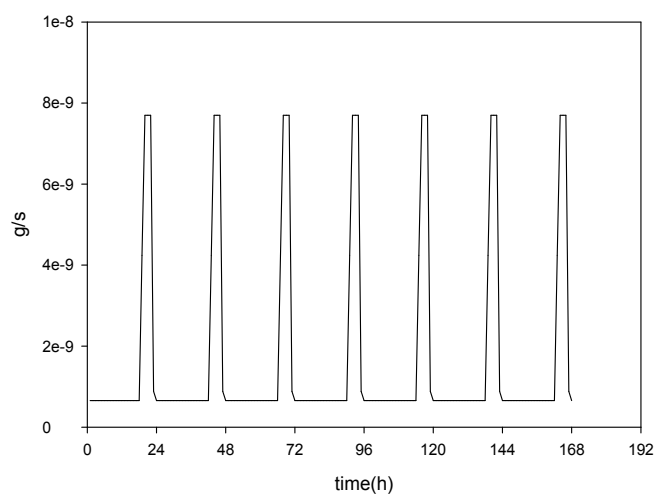
## 7. Simulation of PBDEs in indoor space in South Korea

### (1)BDE 47

As introduced in previous part, there is few literature and papers has monitored the concentration of PBDEs in indoor space in South Korea, Therefore, in this study, How Penta-BDEs concentration varied in different three indoor spaces is the one important focus in this study.

The simulation period is initialized as 7 days The initial information is from the statistic administration of South Korea, and through the internet, a survey also used for collecting information for Research office. And all of the data used is the geometric mean value from the raw data. However, even most of the information and data are examined, assumptions is given for prediction as well. All 3 indoor spaces are assumed that the height is 3 meters, since there is no representative data for it, And time of period for using computer is an empirical assumption, since different people has different custom to use their computer which leads to difficulty to summary it.

(a)





Refers to Figure 6-13 Obviously, among three different scenario, the emission rates in internet cafe is the highest, even it has the largest volume of space among three indoor spaces, high computer density still leads to high emission rate.

(c)

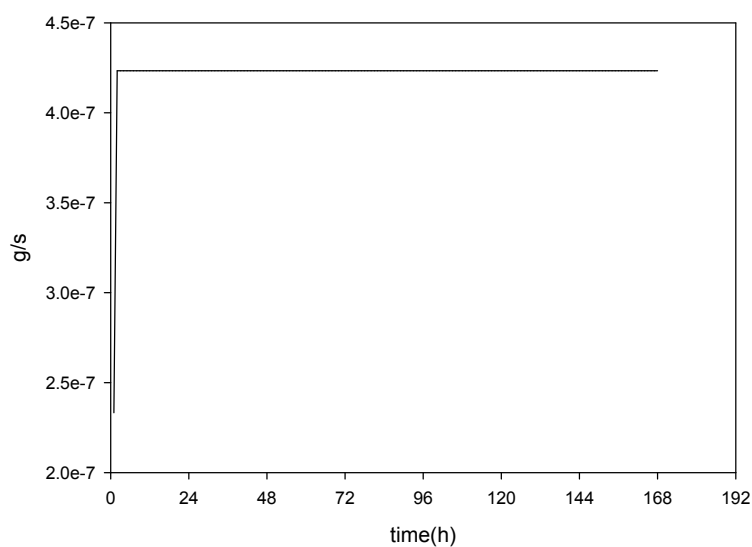
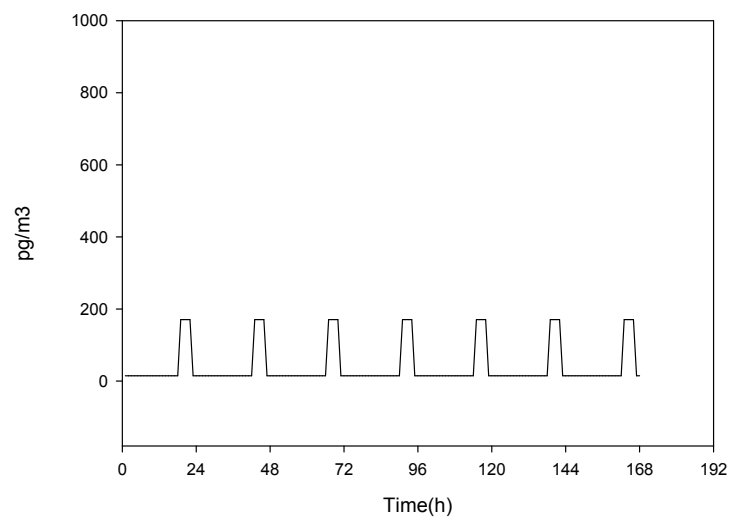
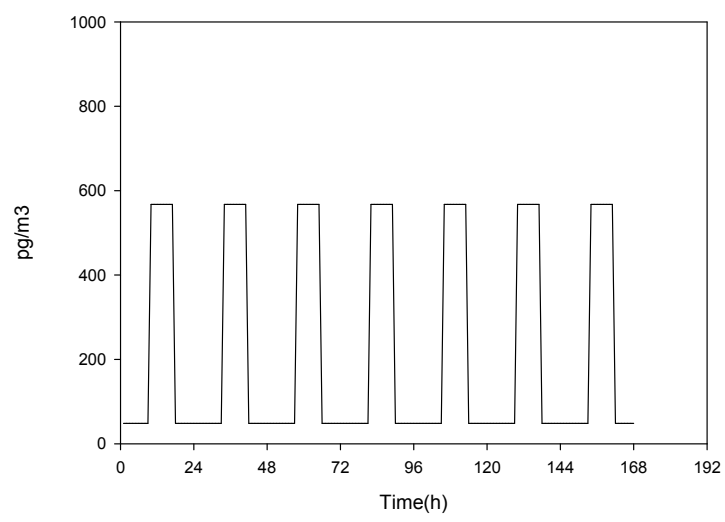


Figure 6-12. (a) emission rates of BDE 47 in home(one computer).  
 (b) emission rates of BDE 47 in office(10 computer).  
 (c) emission rate of BDE 47 internet cafe (55 computers).

(a)



(b)



(c)

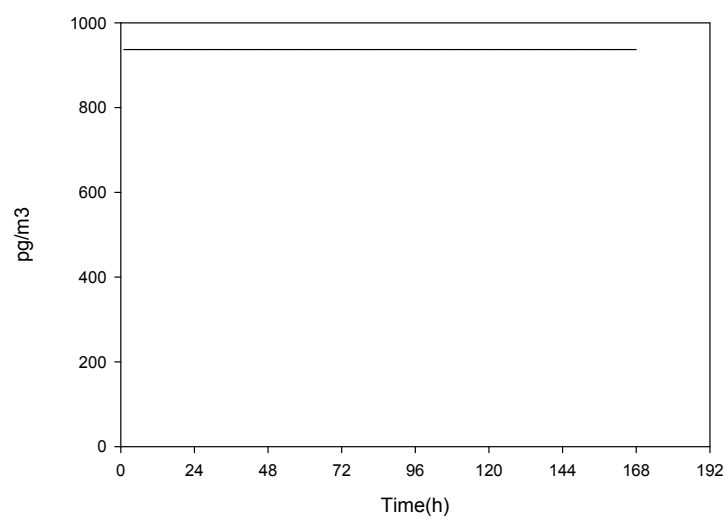


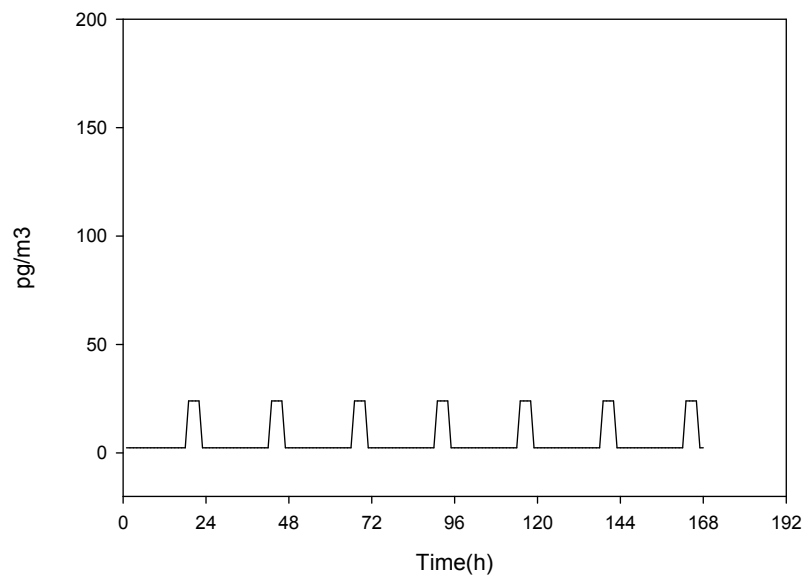
Figure 6-13. (a) BDE 47 concentration with time variation at home  
(b) BDE 47 concentration with time variation in office  
(c) BDE 47 concentration with time variation in internet cafe

According to figure 6-13, the pattern of concentration variation is similar to the pattern of emission source, which indicates that emission from computer is the dominant factor which impacts on the concentration of BDE 47 in each indoor spaces. Higher density of emission source and operating computer in long time, will lead to high risk of human exposure to PBDEs. As figure 6-13(c) shows, since the computer keeps on all day long in internet cafe, the concentration level of BDE 47 maintains high in spite of mechanical ventilation operated all day long.

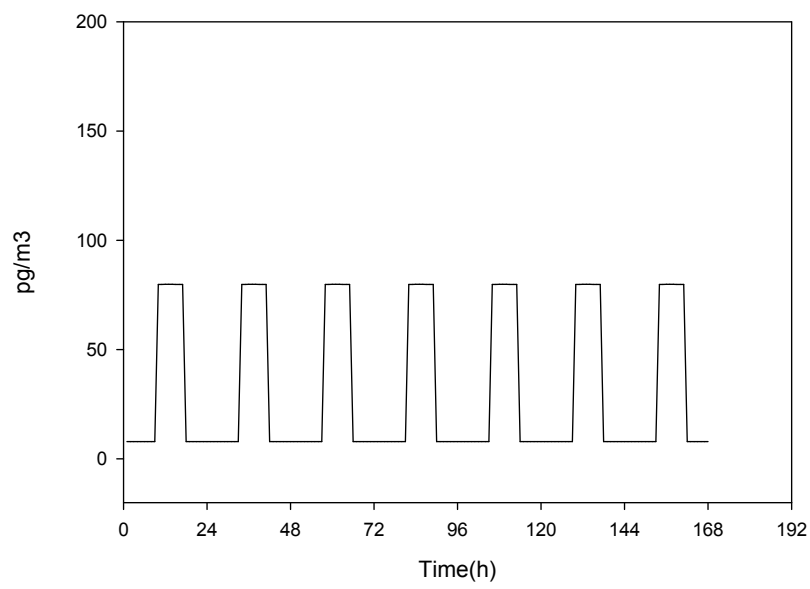
As demonstrated above, according to the results of prediction, ventilation process result in relieving the remain chemical in indoor space, however, the effect is apparent once the outdoor PBDEs concentration in atmosphere is low. Geometric mean of BDE 47 concentration in each spaces are calculated as 22pg/m<sup>3</sup>, 110pg/m<sup>3</sup>, 938pg/m<sup>3</sup>(sum of vapor and particle phase ) at home, research office and internet cafe respectively. The BDE 47 concentration in internet cafe is about 9 times higher than which in research office and nearly 45 times higher than which at home. As expected, the exposure risk is highest in internet cafe, and lowest in home

(2)BDE 99

(a)



(b)



(c)

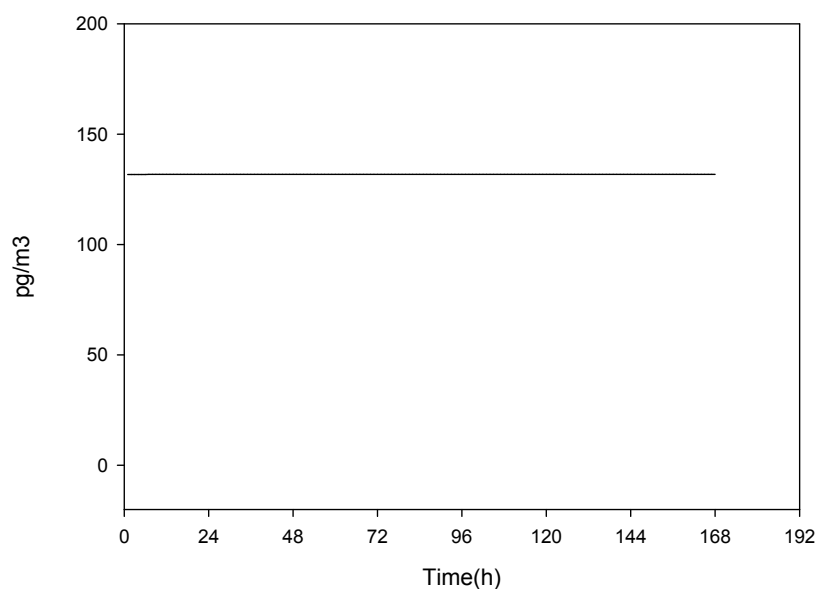
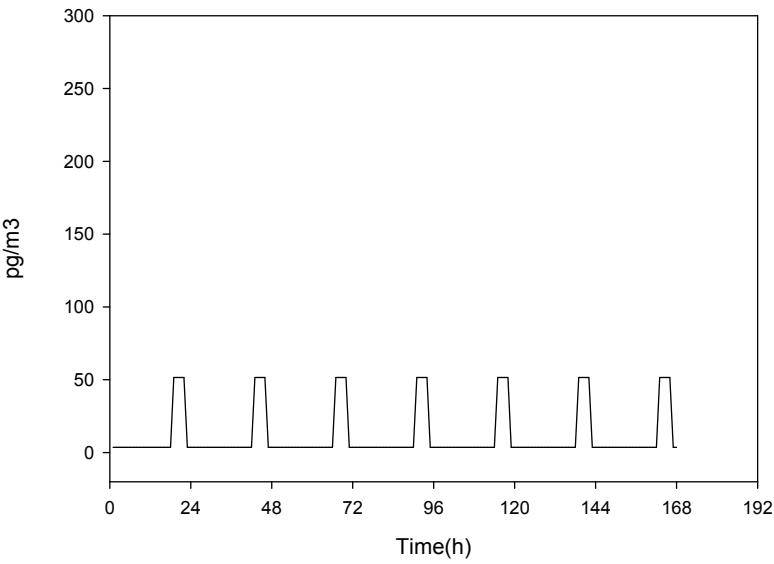


Figure 6-14. (a) BDE 99 concentration with time variation at home  
(b) BDE 99 concentration with time variation in office  
(c) BDE 99 concentration with time variation in internet cafe

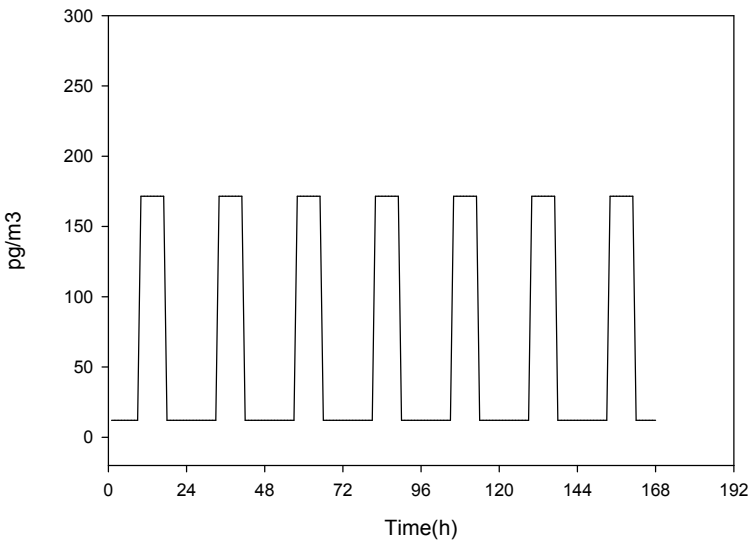
Concentration of BDE 99 shows the similar pattern with which of BDE47. The geometric mean value of concentration at home, office and internet cafe are 3.49pg/m3, 17.1 pg/m3, 132pg/m3 respectively. BDE 99 concentration in internet cafe is about 8 times higher than in office and 45 times higher than in the office. Compares to BDE 47, the concentration of BDE 99 is much lower.

(3)BDE 100

(a)



(b)



(c)

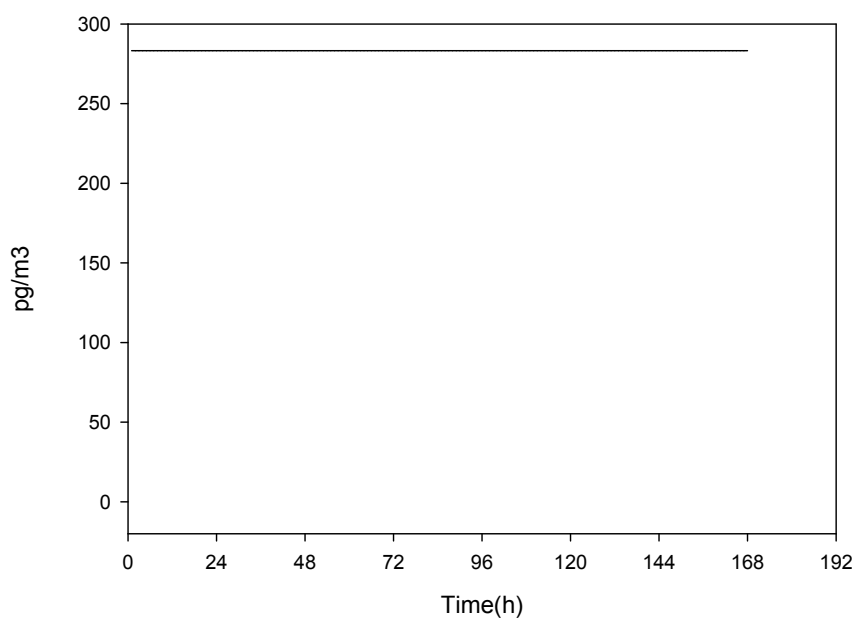


Figure 6-15. (a) BDE 100 concentration with time variation at home  
(b) BDE 100 concentration with time variation in office  
(c) BDE 100 concentration with time variation in internet cafe

Concentration of BDE 100 is also similar with which of BDE47 and BDE 99. The geometric mean value of concentration at home, office and internet cafe are 5.6pg/m3, 29.3 pg/m3, 283pg/m3 respectively. BDE 100 concentration in internet cafe is about 10 times higher than in office and 55 times higher than in the office. The concentration level is similar with BDE 99, but about 5times lower than BDE 47.



## 7. Conclusions

Previous IIAQ model is modified for more accurate prediction for PBDEs, The emission rate from computer is designed as a function of temperature, which is more close to what happens in real world.

And the modified model was estimated by comparing the result of similar scenario in a monitoring paper and simulation, Even that slightly variation exist, the simulation result is considered acceptable which means modified IIAQ model is convinced for following simulation.

The concentration of BDE 47, BDE 99, BDE 100 with computer operating is calculated as 1070%, 906%, 1320% higher than which without computer operating. This outcome is adapt to the result from published thesis(Waye, 2008) By comparing the concentration of BDE 47 with doors and windows open and not, it is stated that ventilation may plays a minor role on relieving indoor PBDEs concentration once the outdoor concentration of chemical is in same level with which in indoor environment. However, if large differences between PBDE concentration in out door air and indoor air, ventilation process can decrease about 11.3% PBDEs in indoor environment. Even that higher internal temperature of computer leads to higher emission of PBDEs to indoor air, increasing indoor temperature result in lower PBDEs concentration in indoor environment. Concentration of TSP in indoor and outdoor environment will also give effects on PBDEs concentration in indoor environment, especially effects on deposition process and indirectly varies the concentration of PBDEs in indoor dust. However, in this thesis, PBDEs concentration in dust is not the focus, it

can be researched in future study.

The simulation result of three indoor spaces is followed by which expected, emission source is the dominant factor that effects on PBDEs concentration in indoor environment. And internet cafe is the place with the highest exposure risk to people among the three indoor environment.

However, many emission source of PBDEs are existed in indoor environment, such as electric appliance, textiles, PUF-contained furnitures, and so forth in actual. Due to lack of accurate data and information of these emission sources, they are not considered in modified IIAQ model, which may leads to imprecision of prediction.

In future study, in order to complete the IIAQ model, more PBDEs congeners should be estimated in this model, and if there are available information of other emission sources, consider them in modified IIAQ model will result in more exact prediction.

## ■ Reference

- 설경(2008) IIAQ 모형을 이용한 실내 미세 먼지 관리 방안 - 실외 대기질과 실내 오염원의 영향-, Master D. Dissertation Seoul National Univ.
- Adrian Covaci, Stuart Harrad, Mohamed A.-E. Abdallah, Nadeem Ali, Robin J. Law,Dorte Herzke, Cynthia A. de Wit (2011) “Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour”, *Environment International*, 37: 532-556.
- Alexander Wong, Ying Duan Lei, Mehran Alaei, and Frank Wania, (2001) “Vapor Pressures of the Polybrominated Diphenyl Ethers” *J. Chem. Eng. Data*, 46, 239-242
- Anna Palm, Ian T. Cousins, Donald Mackay, Mats Tysklind, Chris Metcalfe, Mehran Alaei (2002) “Assessing the environmental fate of chemicals of emerging concern: a case study of the polybrominated diphenyl ethers”. *Environmental Pollution*, 117:195-213.
- Anubhagoel, Laural (2006) “Spray Irrigation of Treated Municipal Wastewater as a Potential Source of Atmospheric PBDEs” *Environ. Sci. Technol.* 40, 2142-2148
- Baoqing Deng & Ruixue Tian & Chang Nyung Kim (2007) “An analytical solution for VOCs sorption on dry building materials” *Heat Mass Transfer*, 43: 389 - 395.
- Banu Cetin, Mustafa Odabasi (2005) “Measurement of Henry’s Law constants of seven polybrominated diphenyl ether (PBDE) congeners as a function of temperature”, *Atmospheric Environment*, 39:5273-5280.
- Charles J. Weschler, William W. Nazaroff (2008) “Semivolatile organic compounds in indoor environments”, *Atmospheric Environment*, 42: 9018-9040.
- Cynthia A. de Wit (2002) “An overview of brominated flame retardants in the environment”, *Chemosphere*, 46: 583-624.
- Duohong Chen, Xinhui Bi, Ming Liu, Bo Huang, Guoying Sheng, Jiamo Fu (2011) “Phase partitioning, concentration variation and risk assessment of polybrominated diphenyl ethers (PBDEs) in the atmosphere of an e-waste recycling site”. *Chemosphere*, 82: 1246-1252.
- EPA (2010) “An exposure assessment of Polybrominated diphenyl ethers” National Center for Environmental Assessment Office of Research and Development U.S. Environmental Protection Agency Washington,

- Anubha A Goel, Laura L LL McConnell, Alba A Torrents, Joseph R JR Scudlark, Staci S Simonich (2006), "Spray irrigation of treated municipal wastewater as a potential source of atmospheric PBDEs." *Environ Sci Technol* 40(7):2142-8
- Hermann Fromme, Wolfgang Körner, Nabil Shahin, Antonia Wanner, Michael Albrecht, (2009)"Human exposure to polybrominated diphenyl ethers (PBDE), as evidenced by data from a duplicate diet study, indoor air, house dust, and biomonitoring in Germany" *Environment International* 35: 1125-1135.
- Hidetaka Takigami, Go Suzuki, Yasuhiro Hirai, Yukari Ishikawa, Masakiyo Sunami, Shin-ichi Sakai (2009)"Flame retardants in indoor dust and air of a hotel in Japan" *Environment International* 35: 688-693
- Isao Watanabe, Shin-ichi Sakai (2003) "Environmental release and behavior of brominated flame retardants", *Environment International*, 29:665-682.
- James F. Pankow (1993) "An absorption model of gas/particle partitioning of organic compounds in the atmosphere", *Atmospheric Environment*, 28:185-188.
- Jingwen Chen, Degao Wang, Shuanglin Wang, Xianliang Qiao, Liping Huang (2007) "Quantitative structure-property relationships for direct photolysis of polybrominated diphenyl ethers", *Ecotoxicology and Environmental Safety*, 66:348-352.
- John D. Meeker, Paula I. Johnson, David Camann, Russ Hauser (2009) "Polybrominated diphenyl ether (PBDE) concentration in house dust are related to hormone levels in men", *Science of the Total environment*, 407: 3425-3429.
- Karin Vorkamp, Marianne Thomsen, Marie Frederiksen, Marie Pedersen, Lisbeth E. Knudsen (2011) "Polybrominated diphenyl ethers (PBDEs) in the indoor environment and associations with prenatal exposure", *Environment International*, 37:1-10.
- Ki-In Choi, Suk-Hui Lee, Masahiro Osako (2009) "Leaching of brominated flame retardants from TV housing plastics in the presence of dissolved humic matter", *Chemosphere*, 74:460-466.
- Lee, Dong-Soo & Won, Doyun. (2007). "integrated Indoor Air Quality Model" Not published.

- Leisa-Maree L. Toms, Laurence Hearn, Karen Kennedy, Fiona Harden, Michael Bartkow, Christian Temme, Jochen F. Mueller (2009) "Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air" *Environment International* 35, 864-869.
- Lesliam Quiros-Alcala, Asa Bradman, Marcia Nishioka, Martha E. Harnly, Alan Hubbard, Thomas E. McKone, Brenda Eskenazi (2011), "Concentrations and loadings of polybrominated diphenyl ethers in dust from low-income households in California", *Environment international*, 37:592-596.
- Micheal Martin, Paul K.S. Lam, Bruce J. Richardson (2004) "An Asian quandary: where have all the PBDEs gone", *Marine Pollution Bulletin*, 49:375-382.
- Mehran Alaei, Pedro Arias, Andreas Sjödin, Ake Bergman (2003) "An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release", *Environment international*, 29:683-689.
- Robin J. Law, Dorte Herzke, Stuart Harrod, Steven Morris, Philippe Bersuder, Colin R. Allchin (2008) "Levels and trends of HBCB and BDEs in the European and Asian environments, with some information for other BFRs". *Chemosphere*, 73:223-241.
- Stuart Harrod, Catalina Ibarra, Miriam Diamond, Lisa Melymuk, Matthew Robson, Jeroen Douwes, Laurence Roosens, Alin Constantin Dirtu, Adrian Covaci (2008), "Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States" *Environment International* 34, 232 - 238.
- Scot Kenyon Waye (2008), "Inhalation exposure Pathway for Polybrominated diphenyl ethers: a source for human receptor model for semivolatile organic compounds" The University of Texas at Austin
- Stuart Harrod (2006) "Concentrations of Polychlorinated Biphenyls in Indoor Air and Polybrominated Diphenyl Ethers in Indoor Air and Dust in Birmingham, United Kingdom: Implications for Human Exposure", *Environ. Sci. Technol.* 40, 4633-4638
- Stuart Harrod (2004) "Preliminary Assessment of U.K. Human Dietary and Inhalation Exposure to Polybrominated Diphenyl Ethers" *Environ. Sci. Technol.* 38, 2345-2350.
- T. Gouina, T. Harner (2003), "Modelling the environmental fate of the

- polybrominated diphenyl ethers" *Environment International* 29, 717 - 724.
- Tom Harne and Mahiba Shoeib(2002) "Measurements of Octanol-Air Partition Coefficients (KOA) for Polybrominated Diphenyl Ethers (PBDEs): Predicting Partitioning in the Environment", *J. Chem. Eng. Data*, 47, 228-232
- Wendy D'Hollander, Laurence Roosens, Adrian Covaci, Christa Cornelis, Hans Reynders, Karen Van Campenhout, Pim de Voogt, Lieven Bervoets(2010)"Brominated flame retardants and perfluorinated compounds in indoor dust from homes and offices in Flanders, Belgium", *Chemosphere* 81, 478 - 487.
- Yue Xu, Gan Zhang, Jun Li, Xiang Liu, Xiangdong Li(2011) "Atmospheric polybrominated diphenyl ethers(PBDEs) and Pb isotopes at a remote site in South western China: Implication for monsoon-associated transport", *Science of Total Environment*, 409: 4564-4571.
- Zhishi Guo(2002) "Review of indoor emission source models. Part 2Parameter estimation", *Environment Pollution*, 120: 551-564.

## 국문 초록

PBDE의 유해성은 널리 알려져 있으며 주로 실내의 공기를 통해서 인체에 노출이 되는 것으로 평가되어 왔다. 그럼에도 불구하고 국내의 다양한 실내 환경에서 PBDE의 오염도에 대한 측정이 아직 이루어지지 못하고 있고, 실내 공기의 오염도에 미치는 주요 요인이 무엇인지에 대한 체계적 연구가 부족한 실정이다. 따라서 본 연구에서는 주요 실내 환경인 일반가정집, 연구실, 피시방의 공기질을 예측을 통하여 비교하고 각각의 환경에서 PBDE의 오염도에 영향을 미치는 주요 인자들의 역할을 평가하여 오염도를 효과적으로 줄일 수 있는 방안을 제안하고자 하였다.

실내 공기의 PBDE오염도를 예측하기 위해 기존에 개발된 반휘발성 유기화합물(semi-volatile organic compounds) 실내공기질 예측모형인 Integrated Indoor Air Quality (IIAQ) 모형을 사용하였다. 본 연구를 위해 기존의 모형을 수정하였는데, 가장 중요한 수정내용으로는 실내 오염원으로 부터의 배출속도를 온도의 함수로 표현하였다는 점이다. 또한 simulation 기간 중에 환기시기를 선택할 수 있도록 개선하였다. 이어서 IIAQ모형에 의한 예측치의 신뢰도를 확인하기 위해 예측값을 기존의 측정값과 비교하였다. PBDE로는 BDE47, BDE99 BDE100을 연구 대상으로 선정하였다. 모형에서 일반가정집의 공간크기는  $5*3*3\text{ m}^3$ , 오염원(컴퓨터)은 1대, 연구실은  $9*5*3\text{ m}^3$ , 오염원 10대, 그리고 피시방은  $15*10*3\text{ m}^3$ 의 크기에 오염원 개수는 55개임을 기본 환경조건으로 사용하였다.

BDE47, BDE99, BDE100 각각에 대한 모형 예측값과 측정값을 비교하여, 개선된 모형을 평가 한 결과, 모형의 예측평균값은 측정평균값과 2배 범위 안에서 일치하는 것으로 나타나 모형의 예측치는  $\pm 100\%$  수준의 불확실성을 가지는 것으로 평가되었다. 기본 환경조건에서 모형 예측 결과에 따르면, 정상상태에 도달한 BDE47 농도는 일반 가정집에서  $22\text{ pg/m}^3$ , 연구실에서  $110\text{ pg/m}^3$ , 피시방에서  $938\text{ pg/m}^3$  정도의 수준이었다. BDE99는  $17.1\text{ pg/m}^3$ ,  $33\text{ pg/m}^3$ ,  $132\text{ pg/m}^3$ 로 각각 예측되며 BDE 100의 경우에는  $5.6\text{ pg/m}^3$ ,  $29.3\text{ pg/m}^3$ ,  $283\text{ pg/m}^3$ 로 각각 예측되었다. 이 결과에 따르면 피시방의 농도가 일반가정집에 비하여 약 50배 이상이 될 수도 있는 것으로 나타나 노출 시간이 같다면 가장 높은 수준의 노출이 일어날 수 있는 공간이 될 수 있음을 알 수 있다. Penta-BDEs의 실내공기 중 농도 수준에 영향을 미치는 인자로서, 우선 컴퓨터 사용여부가 매우 중요한 것으로 나타났는데 예를 들면, 컴퓨터가 지속적으로 켜져 있는 경우의 정상상태 농도는 꺼져 있을 때 보다 PBDE에 따라

9~13배 정도 큰 것으로 예측되었다. 이는 켜져 있는 경우 컴퓨터 내부의 온도가 상승하게 되고 그에 따라 PBDE의 배출속도가 증가하기 때문이다. 또한 공기의 환기 속도도 대단히 중요한 인자일 것으로 예상되었으나 그 영향의 크기는 실내공기 중의 PBDE농도와 유입되는 공기 중의 PBDE 농도의 차이에 따라 다르게 나타났다. 즉, 일반가정집의 경우, Penta-BDEs 실내농도가 낮아서 일반적인 실외농도와 차이가 별로 없기 때문에 환기의 효과는 그다지 크지 않다. 반면에 연구실이나 피시방 같은 경우는 실내외 Penta-BDEs 농도 차이가 보다 크기 때문에 환기의 효과가 좀 더 뚜렷하다. 예를 들어 환기율을 0.5/day로 하는 경우 연구실과 피시방에서 각각 11.3%, 45%의 정상상태 농도 감소효과가 있는 것으로 예측되었다. 한편 실외 대기의 Penta-BDEs의 농도가 실내 공기 중의 농도의 100배 이상 높을 때 환기에 의해 실내 Penta-BDEs 농도를 증가 시키는 효과가 뚜렷하게 나타났다. 이와 같은 요인들을 종합하면, 피시방의 오염도가 높은 이유는 기본적으로 PBDE의 주요 배출원인 PC의 수가 실내 환경의 단위 부피당 가장 많기 때문이고, 더불어 PC가 켜져 있는 시간이 길고 그에 따라 온도도 높게 유지되어 각 PC의 PBDE 배출속도도 가장 크기 때문인 것으로 판단할 수 있다. 한편 이러한 요인들과는 달리 피시방의 경우 환기에 의해 농도가 상당히 감소될 수 있는 여지가 있지만 환기의 농도저감효과를 감안 한다면이라도 일반적인 환기율 범위 안에서는 전반적으로 농도는 높게 유지될 가능성이 크다는 것을 알 수 있다.

컴퓨터가 가장 주된 PBDE 배출원인 조건하에서 실내공기질에 영향을 미치는 주요 요인으로서 컴퓨터의 밀집도, 켜놓았는지 아닌지의 상태를 들 수 있다. 켜 놓은 경우에 PBDE 오염도의 차이가 10배 이상이 될 수도 있는 것으로 나타났는데, 이는 온도의 상승에 기인하는 것이기 때문에, 실제 사용하지 않는 경우에는 반드시 끄는 것이 에너지 절약뿐만 아니라 PBDE에 대한 노출을 줄이는데 큰 도움이 될 것으로 판단된다. 또한, 컴퓨터의 밀집도가 어느 정도 이상이 되고 사용시간이 길어지는 경우에는 PBDE에 대한 노출을 줄이기 위해서는 적극적인 환기를 하는 것이 효율적인 방안이 될 수 있을 것이다.

Key words: PBDEs, Penta-BDEs, Polybrominated diphenyl ethers, indoor, concentration, indoor model

Student number: 2010-24185